

Fig 51a. Balloon Pattern Daniell Cell.
(Siemens Brothers & Co, Ltd)

PRACTICAL PRIMARY CELLS

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"ELECTRIC LIGHTING, STARTING, AND IGNITION FOR MOTOR VEHICLES"

"ELECTRIC WIRING DIAGRAMS FOR MOTOR VEHICLES"



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PREFACE

THE purpose of this little book is to give working details of those cells having the greatest practical value, both for the laboratory and for commercial purposes.

As the Voltaic cell was the first practical source of current, so, we may speculate, some greatly perfected form of cell may, in the future, replace the dynamo as the ultimate source of electrical power

A great many different types of cell have been evolved during the past century, the greater number being at most scientific curiosities. The author has endeavoured to weed out from this mass of detail those cells which can really be used with some satisfaction for the purposes required, and in each case to add data of their performance, a feature hardly ever published in existing textbooks, so that the user may know what output to expect from each type of cell

In order that the reader may keep in touch with many of those cells which may be of interest but which for some reason or another have become obsolete, an index of cells has been added at the end of the book giving the main details of the constituents of such cells as have fallen into disuse, also references as to where fuller particulars can be found

The author wishes to thank the Silvertown Co., Messrs Siemens Bros & Co., and other manufacturers, for the loan of electros, etc., and to the Atlas Carbon and Battery Co. for help in experimental work for several years past

A MORTIMER CODD

ESHER, 1929

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INSET PLATE

BALLOON PATTERN DANIELL CELL (Siemens) *Frontispiece*

PRACTICAL PRIMARY CELLS

CHAPTER I

THE SIMPLE VOLTAIC CELL

THE earliest primary cell is the simple element devised by Volta in 1793. This consists of a vessel containing dilute acid, in this case dilute sulphuric acid, into which dip two strips of metal, one of zinc, the other of copper (Fig. 1). The liquid is called the electrolyte, and the strips the electrodes.

When these metal plates are introduced into the electrolyte the copper plate shows no apparent action, but the zinc will be attacked by the sulphuric acid giving off bubbles of hydrogen at the zinc plate and forming zinc sulphate in the solution.

If a sensitive voltmeter be applied between the ends of the strips there will be found to exist between them a difference of pressure of about 1 volt.

The ends of the strips projecting above the electrolyte may be regarded as the poles of the cell, and the voltmeter (if a moving coil instrument) will show that the copper strip forms the positive or + pole, and the zinc strip the negative or - pole, that is, current is flowing through the voltmeter or exterior circuit from the copper to the zinc electrode.

If, however, we regard the flow of current from the point of view of the interior of the cell we see the current is flowing from the zinc to the copper, that is, the zinc is electro-positive to the copper, whereas the copper is electro-negative to the zinc.

If we substitute for the electro-positive electrode or zinc a plate of magnesium we shall obtain a voltage of the order of 1.7 volts, if aluminium is used a voltage of about .45, or with iron about 4 volts

Suppose now we remove the copper electrode and substitute a carbon plate, using the original zinc we get a voltage

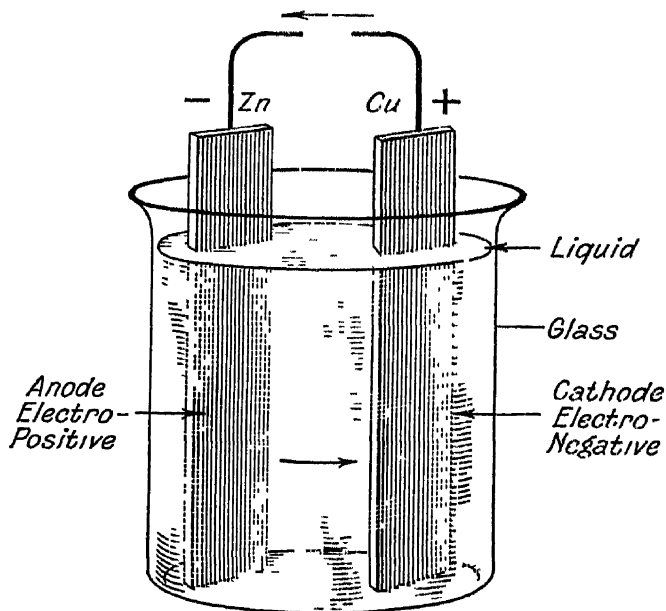


FIG 1 SIMPLE VOLTAIC CELL

of 1.04, with magnesium a voltage of about 1.9, with aluminium about .59, and with iron .52 volts.

From this we see some metals or bodies are more electro-positive than others, and also in relation to themselves

In this way we can build up a relative table of chemical elements arranged in their various relationships one to another, as shown on page 3

We observe from this table that iron is electro-positive to lead and nickel to gold, etc., so that the farther apart

ELECTRO-CHEMICAL SERIES*

Electro-positive end—		<i>Difference in potential in air for various metal couples (Ayrton and Perry)</i>	
Potassium		Zinc	} 210
Sodium		Lead	
Magnesium		Tin	069
Aluminium		Iron	313
Chromium		Copper	146
Manganese		Platinum	238
Zinc		Carbon	113
Iron			
Cobalt			
Nickel		Zinc carbon =	<u>1 089</u>
Lead			
Cadmium			
Tin			
Bismuth			
Copper			
Hydrogen			
Mercury			
Silver			
Antimony			
Gold			
Iridium			
Platinum			
Carbon			
Boron			
Nitrogen			
Arsenic			
Selenium			
Phosphorus			
Sulphur			
Iodine			
Bromine			
Chlorine			
Oxygen			
Electro-negative end— Fluorine			

we can choose our electrodes, other things being compatible, the greater the electrical pressure the cell will generate.

Returning to our zinc-sulphuric acid-copper cell, we have seen that it generates on open circuit a pressure of about 1 volt

* Some rarer elements are omitted for brevity It should be noted also that the series vary slightly under different conditions

Suppose now we close the outer circuit through some load, such as a good electric bell in circuit with an ammeter.

For the first moment there will be a heavy rush of current and the bell will ring well, but after the first second or two the current will steadily fall until the bell will either cease to work or only emit a faint tinkle. If, under these circumstances we examine the cell we shall find not only that the zinc is still emitting bubbles, but that the copper plate is becoming coated with a fine layer of bubbles also.

If these bubbles are removed by stirring the copper plate, or better, by removing it and wiping it, the same cycle of events will occur, the current momentarily rising only to fall as the bubbles form on the copper surface.

The formation of these bubbles, which are of hydrogen gas, constitutes what is known as "polarization."

Now a voltaic cell is an arrangement wherein there is a direct transformation of chemical into electrical energy, and, broadly speaking, the more violent the reactions the greater the energy produced.

Of the two electrodes it seems necessary that one alone should be attacked, the second simply serving to form the electro-negative electrode and to collect the current from the cell, presenting a positive pole to the exterior circuit.

The reason for the formation of the bubbles upon the copper plate of the cell will appear simpler if we consider the theory of Grotthuss and Clausius

This theory assumes that the molecules of the electrolyte have their atoms charged electro-positively and negatively respectively

In an ordinary solution the molecules may be visualized as lying about or even moving in a higgledy-piggledy manner (Fig 2).

As soon, however, as the circuit is closed, the molecules

as it were stand to attention and form a chain, the hydrogen ends being turned toward the electro-negative or copper plate, and the other ends towards the zinc plate. As long as a current flows there is assumed to be an interchange of partners along the chain.

Under these circumstances we can see that the SO_4 will combine with the zinc plate to form zinc sulphate (ZnSO_4), while hydrogen will be freed at the copper plate

Faraday named the electrode by which the current

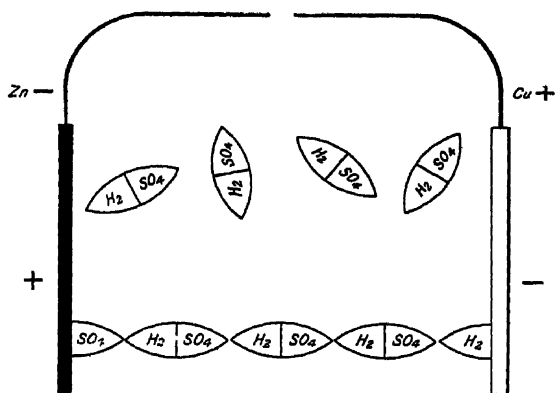


FIG 2 GROTHUS CHAIN, ZINC—SULPHURIC ACID—
COPPER

enters a cell (in this case the zinc), the anode, and that by which it leaves the cathode, also those atoms which have been sundered and carried towards the cathode, cations, those remaining at the anode, anions

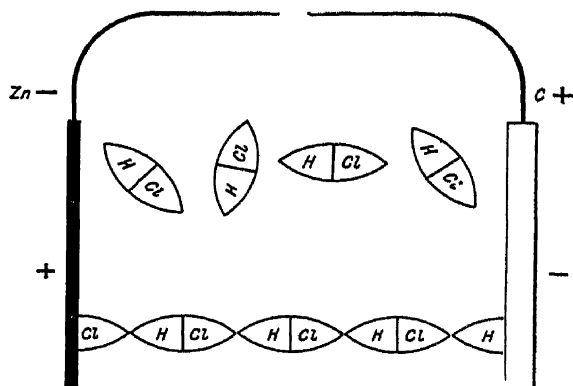
Hydrogen and the metals may be regarded as cations, since they seem to move toward the cathode, chlorine and oxygen as anions

We have seen that if we substitute an element in the electro-chemical series more widely separated from zinc, such as carbon, we shall obtain different results, thus, when using carbon against zinc in dilute sulphuric acid the voltage is rather over 1 volt, with magnesium about

1.9 volts, with aluminium about 6 volts, and with iron .52 volts, as was to be expected

Now instead of using dilute sulphuric acid we may, with a zinc carbon couple, use dilute hydrochloric acid without any appreciable change of voltage.

As previously described, the Grotthus chain works out as in Fig 3, hydrogen being evolved at the carbon cathode and zinc chloride at the anode, and also as before the hydrogen film developed on the carbon causes a drop in current



due to polarization, but this time not quite so rapid as with the copper plate, for reasons we will afterwards explain

Depolarization.

Our first experiment has shown that when the hydrogen bubbles begin to form on the surface of our copper or carbon electrode the current begins to fall.

The reason is twofold, first, the lodgment of bubbles increases the internal resistance of the cell by lessening the exposed surface of the plate, and, secondly, hydrogen itself being electro-positive, tends to set up an opposing electrical pressure.

Clearly, if the cell is to be of any practical use we must devise means whereby polarization can be eliminated

This can be effected by three methods—

- 1 Mechanical.
- 2 Chemical
- 3 Electro-chemical

The first, or mechanical, method was also the earliest to be tried, and in the Smee cell arrangement consisted of a silver plate coated with finely-divided platinum, from the surface of which the hydrogen bubbles parted more or less freely. Walker suggested that the rough surface of a carbon plate platinized would aid depolarization, and so to a certain extent it does. In our experiment with the simple cell, using carbon, the voltage was stated to be about 1.04, but when first the carbon plate is inserted the voltage shown is about 1.3 volts. This higher voltage is to some extent due to the superior depolarizing surface of the rough carbon over the smooth copper, but not wholly so. It is noticeable that with the carbon the bubbles rise in a stream to the surface much more readily than with the copper as an electrode.

Other means of mechanical depolarization suggested have been moving the plates in solution by clockwork, brushing the plates mechanically, using wire gauze to disengage the bubbles, and using circular rotating plates half immersed in the solution, so that the exposed half was depolarized in the air.

In the Velvo carbon cell, carbon rods formed into a flat grid are covered with a coating of velveteen cemented on and carbonized. From this large surface the hydrogen bubbles are readily disengaged, but the voltage is rather low (about .8 volt) and the surface delicate.

The second, or chemical, method consists in adding to the electrolyte some highly-oxidizing substance which will combine with the hydrogen while it is still in a nascent state, or the substance added may have a great affinity

for hydrogen, such as chlorine, bromine, and iodine, or may be a metal salt of which the acid radicle will combine with the hydrogen, setting the metal free.

Reverting to the experiment in which we use the carbon rod as cathode, we have seen the initial voltage to be in the neighbourhood of 1.3 volts. Now this voltage is not altogether due to the superior roughness of the carbon surface over that of copper, but is attributable to the well-known fact that carbon is capable of occluding large quantities of gas, in this case air rich in oxygen, and it is the oxygen occluded within the carbon plate which is responsible for the relatively high initial reading.

Maiche took advantage of this fact in constructing his cell, in which he used lumps of platinized carbon semi-submerged in the electrolyte and revived by the oxygen of the air. In recent years a very successful class of cells has sprung up, depending upon the air as depolarizer, "air depolarizing" cells, which will be dealt with later.

Amongst chemical depolarizers added to the solution, Poggendorff, Grenet, Fuller and others have used bichromate of potash or soda or chromic acid itself, and Dun has used potassium permanganate. Grove, Bunsen, and Callan suggested nitric acid, Leclanché and Lalande the solid depolarizers manganese dioxide and copper oxide respectively, and Reynier, Fitzgerald, and Harrison lead peroxide.

Upwood constructed powerful cells in which chlorine gas was pumped round the carbon electrodes, but such cells are impracticable for everyday use. Figuier, Duchemin, Fabst, Paine, d'Arsonval, and Darimont have employed ferric chloride as a depolarizer, the active principle in this case being the chlorine. Niaudet replaced the manganese dioxide of Leclanché by chloride of lime (bleaching powder), but such a cell gives poorer results and has an unpleasant smell. Many other substances have from time to time been suggested either alone or more generally in conjunction

with some other depolarizer, but, generally speaking, apart from a certain theoretical fancifulness these derivations are worthless.

We now come to the electro-chemical means of depolarization in which some metal, such as copper, mercury, or silver, is freed instead of the hydrogen bubbles, the arrangement being somewhat analogous to an electroplating bath reversed. Such cells are the Daniell, the Marié Davy and Schanschieff, and the de la Rue respectively, however, all except the Daniell are practically extinct owing largely to the cost of material. These cells will be dealt with later in their appropriate places.

Local Action.

In our simple cell we have seen that when the zinc electrode is immersed in the solution a certain action takes place, the zinc being dissolved and hydrogen gas evolved.

This action takes place even when the circuit is not closed and, therefore, it is only a question of time before either the zinc is entirely dissolved or the electrolyte used up. If chemically pure zinc could be used there would be little or no action on the zinc, the difference in the behaviour of pure and commercial zinc being due to the impurities contained in the latter. Commercial zinc contains minute impurities of iron, cadmium, arsenic, etc., which act as electro-negative electrodes and set up small local couples which tend to consume the zinc; this is known as local action. If the cell is to give its output in a run of a few hours' duration local action does not greatly matter, beyond the fact that it also tends to exhaust the electrolyte to some extent, but should the cell be intended for open-circuit work, such as for ringing bells, working signals, wireless apparatus or the like, in which its life may extend over months, then naturally any excessive local action would be fatal. Local action cannot be entirely eliminated even by the use of comparatively mild salts,

such as sal-ammoniac instead of acids, for, if precautions are not taken, even with such relatively inactive salts, local action will continue although, perhaps, more slowly. The only exception to this is in cells using an alkaline electrolyte, such as the Lalande cell

Amalgamation.

Kemp, and afterwards Sturgeon, pointed out that if the surface of the zinc electrode is amalgamated with mercury,¹ local action is greatly minimized, and the zinc plate rendered almost immune from the attack of any normal acid on open circuit.

The exact reason for amalgamation having this effect appears obscure

One theory is that the mercury flowing over the surface of the zinc forms a covering to the small particles of impurity, and thus prevents the formation of small local cells tending to feed on the zinc

Others maintain that the impurities float to the surface of the film of mercury, and by ceasing to touch the zinc are rendered harmless. This latter certainly seems to the author the more probable explanation, but there remains the peculiar fact that mercury is electro-negative to zinc, and that instead of setting up increased local action as an additional impurity it actually acts as a palliative.

The writer is inclined to take the view that the zinc in the process of amalgamation floats to the surface of the film of mercury, and as the zinc is used up further supplies of zinc are dissolved and fed up through the mercury film itself, which is thus acting only as a vehicle for presenting *pure* zinc to the action of the electrolyte. This view is confirmed by the fact that zincs amalgamated with a supply of free mercury seem attacked less under similar circumstances than zincs cast with mercury as an amalgam.

There are various ways in which zincs can be amalgamated, the commonest method for laboratory purposes

being to lay the zinc plate in a dish with a little dilute sulphuric acid, and then to rub in a small amount of mercury with a fragment of linen. A fine bright surface will be obtained in this way, but the disadvantage of this method is that when the zinc is stood upright in the cell, after a few hours the mercury drains to the bottom, leaving the top of the zinc open to attack.

Another way is to cast the zinc with up to 5 per cent of mercury as an amalgam.

This has the advantage that as the zinc is dissolved away the remaining mass is more strongly impregnated with mercury. Or, again, the first and second methods may be combined. The zincs used for Post Office Leclanché cells have to contain at least 2.5 per cent of mercury. The addition of too much mercury, although not harmful electrically, renders the zincs very brittle. Another method of amalgamation which has been used in very active solutions, is to cast the zinc in the form of a cup, or inverted telegraph insulator, on the end of an insulated copper rod, which forms the connection. The interior of the cup is filled with an amalgam of zinc heavily impregnated with mercury. As there is slight voltaic action between zinc and zinc amalgam the mercury in the amalgam will eventually spread over the zinc cup itself, thereby protecting it from local action.

The best plan for effecting amalgamation is to make the zinc in the form of a squat cone or pyramid, and place it at the bottom of the cell in company with an ounce or two of free mercury, as in the Fuller cell. Owing to the small height of the zinc the mercury is able to mount over the whole mass of the zinc, giving perfect amalgamation.

In some cases, notably with dry cells, light amalgamation is carried out by adding mercuric chloride to the electrolyte with which the cell is charged, but for ordinary wet cells this method is not so good as ordinary amalgamation with liquid mercury.

It may not be out of place to mention here that aluminium can be amalgamated with mercury by rubbing with a solution of caustic soda. Aluminium so amalgamated shows a rise in pressure of about .5 volt over aluminium unamalgamated, but the disadvantage of so using aluminium is that when amalgamated it forms heavy growths of oxide which eventually choke up the cell. For a few days' use, however, it is quite satisfactory, the best electrolyte being generally a solution of carbonate of soda or potash.

Electromotive Force (E.M.F.) and Potential Difference (P.D.)

We have seen that two dissimilar metals immersed in a suitable solution give a difference in electrification, this, up to the present, we have spoken of as a difference in pressure or voltage, it is, in fact, the electromotive force of the cell (E.M.F.) Electromotive force, then, is that which moves or tends to move electricity. Thus, in our simple cell there is a tendency in the exterior circuit for the current to flow from the point of higher electrification, the copper, to a point of lower electrification, that is, the zinc.

The point of higher electrification is conventionally denoted as the + or positive pole, and the zinc, or point of lower electrification, as the - or negative pole. It will be noted that, theoretically, the E.M.F. is the voltage of the cell on open circuit only, and to ascertain this E.M.F. it would be necessary to employ an electrostatic voltmeter or electrometer. Practically, however, we can measure the E.M.F. on open circuit by using a delicate and high resistance voltmeter, but it must be a voltmeter of high resistance in comparison with the size of the cell measured.

For example, it is useless to attempt to measure the E.M.F. of a small flash-lamp cell, using a cheap watch-type voltmeter taking several milliamperes of current.

In this case all that would be measured would be the working or effectual potential difference (P.D.) of the cell.

because the voltmeter is taking a current comparable with the working load of the cell

In other words, the term E M F expresses the voltage of the cell on open circuit, and the term P D the terminal or working voltage

Let us take two other examples.

First, suppose we measure the voltage of a large central station accumulator cell on open circuit with a sensitive voltmeter Under these conditions we are as nearly as possible measuring its E M F, because the tiny current consumed by the voltmeter bears no relation to the enormous current such a cell is capable of giving. To determine the P.D. of such an accumulator cell we must wait until the cell is discharging at its normal rate

Secondly, take a moderate size Leclanché cell and apply a good voltmeter If the cell is new we shall obtain a reading of about 1.5 volts E M F. on open circuit

Now apply a load of 10 ohms, and it will be found that the voltmeter reads about 1.4 volts—this is the working voltage or P D.

Potential difference is what usually concerns the electrician, but E M F. must also be known for reasons we will shortly outline

Internal Resistance.

In our previous examples we have seen that on applying a 10-ohm load to the Leclanché cell we experienced a certain drop in voltage

If, however, we apply a 10-ohm load to the large accumulator cell no appreciable drop would be measurable The reason for this is that the internal resistance of the accumulator cell is very low indeed, while the internal resistance of the Leclanché cell is appreciable

In the one case we have large plates close together in an excellent conducting electrolyte, in the other we have relatively small electrodes, well separated and having a

porous pot intervening, and a moderately conducting electrolyte only.

The analogy is, in the first case, a large open pipe giving a full bore of water, and in the second a small pipe partially choked with rubbish. Naturally there will be a greater drop in pressure in pounds per sq. in. over the choked pipe than over the larger or open pipe. Yet suppose we stop the flow of water in both pipes by turning off a valve, we shall find that the pressure, when there is no flow of water, is the same in both pipes. This then corresponds to the E.M.F. of a cell when on open circuit.

Generally speaking, then, it is desirable for a cell to have a low internal resistance.

This is naturally governed to a large extent by the particular constitution of the cell itself, but, other things being equal, the cell should have electrodes of large area and an electrolyte which is a good conductor. There should, if possible, be an absence of porous septums, etc., which may interpose resistance and also prevent the electrodes being in close juxtaposition, thereby preventing a strong flow of current.

We have said that, generally speaking, it is desirable for a cell to have a low internal resistance, but the internal resistance of a cell should be chosen so as to have some relation to the external resistance of the circuit.

Up to this point we have alluded to single voltaic elements only as cells. Two or more such cells constitute a battery. The total E.M.F. of the cells when connected in series is the sum of the E.M.F. of the individual cells (Fig. 4). This is also true of the internal resistance of the cells, thus by putting our cells in series we not only increase the E.M.F. available, but we also add to the sum of the total internal resistance.

Suppose now we put our cells in parallel (Fig. 5). In this case the E.M.F. of all cells must be the same, and the total E.M.F. of the battery will only be that of any one

cell, no matter how many are in parallel, but the internal resistance will decrease. In fact, the paralleling of cells is tantamount to constructing one large cell having the same E.M.F., but lower internal resistance (I R). In practice, paralleling cells is generally to be avoided.

Ohm's law teaches us that the current varies directly as the E.M.F., and inversely as the resistance of the circuit.

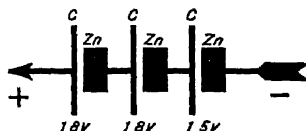


FIG 4. CELLS IN SERIES TOTAL VOLTAGE 5.1 VOLTS

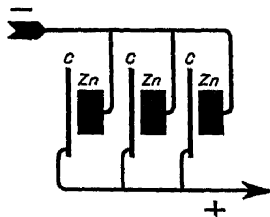


FIG 5 CELLS IN PARALLEL

That is, with an E.M.F. E , applied to a resistance R , a current C will flow,

$$\text{or} \quad C = \frac{E}{R}$$

In the case of a battery working with an exterior circuit of resistance R , it must be understood that R comprehends not only the exterior resistance, but also the resistance of the battery r , therefore we must write

$$C = \frac{E}{R + r}$$

As an example, suppose we have 6 cells in series, each having an E.M.F. of 1.5 volts and an I.R. of 5 ohm, then the total E.M.F., $E = 9$, and the total I.R., $r = 3$. Further, suppose this battery to be used to supply current through a circuit of high resistance, such as an electromagnet or land line, having a resistance of 3600 ohms, then

$$C = \frac{9}{3600 + 3} = \frac{9}{3603} = .0025 \text{ amp approx}$$

It is obvious that the internal resistance of the cells in this case is negligible, and that were it ten times as much the current flowing would not be reduced to any great extent, yet by doubling the voltage we should almost double the current

Another example. The high-tension battery of a wireless set consists of 100 cells, having an E M.F. of 1.5 volts and an I R of 2 ohms per cell. The current consumed is 10 ma, what is the apparent resistance of the exterior anode circuit?

The total E M F. is then 150, and the total I R. 200 ohms

$$\text{Since } R + r = \frac{E}{C}$$

$$R + 200 = \frac{150}{.01} = 15,000 \text{ ohms}$$

therefore the exterior circuit is of approximately 14,800 ohms resistance

Here, again, the I.R. of the cells is of no great account from the point of view of flow of current, but to avoid danger of intercoupling between the valve circuits it is prudent to parallel a reservoir condenser over the battery terminals.

Let us now take an exactly opposite case in which we have four cells of an E M.F. 1.5, and an I R of .5 ohm, as before. The total E M F. being 6 volts, and the I.R. 2 ohms, it is desired to pass a current through an external resistance R of 1 ohm, such as a lamp or valve.

$$\text{Then } C = \frac{6}{1 + 2} = \frac{6}{3} = 2 \text{ amp.}$$

Obviously, if the internal resistance of the cells could be halved the current would rise to 3 amp., and so on until if r was so small as to be negligible the current would be 6 amp.

In such a case the E M F. of the battery would equal its P D , but even with the most powerful primary cell there is an appreciable internal resistance

From these examples the reader will see the importance of choosing the internal resistance in accordance with the work for which the battery is intended

The best results are obtained when the total internal resistance of the battery r equals the total external resistance R

The Becquerel Cell.

If a porous pot containing caustic soda be immersed in a solution of hydrochloric acid, and two similar indifferent electrodes, such as carbon, be inserted, the one inside the pot in the soda and the other outside in the acid solution, we obtain a pressure of just over 7 volt. Such a cell is only capable of furnishing a very weak current, as neither of the electrodes is attacked, the voltage apparently deriving from some interplay of the acid and the alkali within the pores of the porous pot. If, however, zinc and carbon are chosen in suitable solutions, the gain in voltage is very substantial. Unfortunately, porous pots subjected to acid and alkaline solutions simultaneously soon deteriorate and fall to pieces

A somewhat analogous effect is the formation of what is known as a concentration cell within the element itself. Thus, a Leclanché element, after it has been a short time in use, forms zinc chloride, owing to the action of the ammonium chloride on the zinc. This zinc chloride being of heavier density than the ammonium chloride falls to the bottom of the jar, so that the zinc rod is immersed in two solutions, zinc chloride at its foot and ammonium chloride at its top

The result is that the rod tends to be slowly consumed by this locally-formed cell as well as by local action

CHAPTER II

CLASSIFICATION OF CELLS

CELLS may be classified under four headings—

1. True single-fluid cells
2. Single-fluid cells with solid depolarizers.
3. Dry cells.
4. Two-fluid cells

Single-fluid cells of any commercial utility are, hitherto, mostly of the bichromate form, or some variation in which chromic acid plays a part.

Thus nitric acid has been added as in the Fernoy cell, or a mixture of nitro and hydrochloric acid added to chromic acid has been suggested by others. There remains such cells as depend on the oxygen of the air to effect depolarization, and cells which use a particular disposition of ferric chloride both as depolarizer and existant, e.g. Figuer, Pabst, and Codd.

Of the second class there are the Lalande cell having an electrolyte of caustic soda or potash, and a depolarizing plate of copper oxide, also the vast family of the Leclanché variety with its derivations as dry cells. For completeness we must add cells from time to time introduced in which lead peroxide is used, usually in a solution of dilute sulphuric acid.

Of the two-fluid series we begin with the classic Daniell cell, a very perfect cell up to a point, but having several disadvantages.

In this cell a porous pot is usually employed to separate the two fluids, dilute acid or zinc sulphate as the excitant, and a solution of copper sulphate as depolarizer. The main fault in this cell, indeed in any cell using a porous pot, is that osmotic pressure causes the liquid contained in the

pot either to rise or fall according to the arrangement of the liquids, and also there is transference of the contents from either side of the porous diaphragm. In this case copper tends to be deposited upon the zinc, causing local action and drop in E.M.F., while the leaking out of the zinc sulphate tends to weaken the solution of copper sulphate, copper may also be deposited on or in the pores of the porous pot. These details will be dealt with in the practical section.

Another popular cell is the two-fluid bichromate, known as the Fuller. In this cell, instead of mixing the depolarizer (chromic acid) with the excitant (sulphuric acid) directly, the two are separated by a porous pot, resulting in a longer life, but, of course, a higher internal resistance due to the pot. This cell is subject to the same disadvantage as the Daniell and similar cells, in that it is impossible to keep the level on either side of the pot the same. In this class we must also include the Grove and Bunsen cells, rarely used nowadays owing to the unpleasant fumes of the nitric acid. These cells are also subject to a fall in level on the zinc side of the porous pot.

To the two-fluid class must be added the Darimont cell, which employs a solution of ferric chloride outside the porous pot and a particular solution of sodium chloride within. There remains the dry and inert cell class. Although these cells are really special forms of Leclanché cells from Class 2, containing an immobilized fluid electrolyte, they are so important as to necessitate a separate section to themselves.

Osmosis.

If a porous pot be filled with and immersed in a weak solution of acid to the same height there will, naturally, be no tendency for the levels within and without the pot to differ.

If, however, a current is applied by two electrodes

situated within and without the porous wall, a rise in level will eventually be noted in the direction of the current, that is, the level will fall at the anode where the current enters and rise at the cathode where it leaves. This phenomenon is known as electric osmosis.

It will be noted that this phenomenon is exactly similar to that experienced in the Daniell and almost any other two-fluid cell, the excitant falling in the zinc or anode compartment and rising in that of the copper or carbon, that is, the cathode compartment, the current from *within* the cell being, it will be remembered, from zinc to carbon.

The transference of the liquids from one compartment to another does not affect the migration of the ions for, as we have seen, although in the Daniell cell the zinc sulphate falls, yet copper passes from the cathode compartment and is deposited on the zinc. In a similar way in a ferric chloride-sodium chloride cell the sodium chloride falls, yet iron from the outer compartment passes through the interstices of the porous pot, and is deposited upon the zinc.

The author has found that in some cases a state of isosmosis or balance can be established by varying the densities of the two solutions used; thus, if a strong solution of ferric chloride is used in the outer cell and a very strong solution of zinc chloride in the porous pot, hardly any difference in level will take place for many days whether the circuit is open or closed. Still, this fact is not sufficiently certain to render such cells commercially practicable. Varley has already suggested the use of zinc oxide as a lining to the porous pot, and the author has tried impregnating the pores of the pot with prussian blue, soap, gelatine, and the like without much success.

In 1921 Darimont took out a patent for improving the Duchemin cell by adding "an anti acid material, such as powdered chalk, to the exciting solution. As the perchloride of iron penetrates through the wall of the porous vessel a chemical combination takes place between the

perchloride and the chalk, forming an insoluble material which becomes incrustated in the wall of the said vessel, so that this latter soon acts as a porous vessel with a semi-pervious membrane "

In order to prevent the powdered chalk falling to the bottom of the porous pot, the inventor keeps it in suspension in the salt solution by adding a mucilaginous substance, such as cornflour

This cell attained a considerable measure of success, the chief point against it being the necessity to mix two separate chemicals to charge it

Measurements and Testing.

In order to compare the performances of various cells it is necessary to have some standard to which we can work, and which can be applied to any cell

CONSTANT RESISTANCE TEST The most usual method of comparison is to discharge the cell continuously through a 10-ohm resistance, noting the voltage on open and closed circuit periodically, the circuit being broken only momentarily for sufficient time to take the reading on open circuit. Such a test is sufficient for ordinary cells of from 1 to 3 pints, but above this capacity, if the cell is a good one, the length of time necessary to elapse before the exhaustion of the cell becomes tediously protracted, and it is frequently the custom to discharge such large cells through 5 ohms only

On the other hand, for small cells for wireless purposes, 10 ohms would give much too drastic a drain on the cell, so that for these small elements 150 ohms is usually used for a continuous discharge

By taking the open and closed circuit readings (E M F and P D), we are able to calculate the I R of the cell as the test progresses

Thus, if $E = \text{E.M.F.}$ on open circuit, $V =$ the P D on closed circuit, and R the exterior resistance (in this case

10 ohms), we can calculate the internal resistance r of the cell—

$$r = \frac{E - V}{V} R$$

For example, suppose a Leclanché cell gives on open circuit a voltage of 1.24, and on a closed circuit of 10 ohms 1.12 volts, then

$$\text{Internal resistance } r = \frac{1.24 - 1.12}{1.12} \times 10 = 1.07 \text{ ohms.}$$

It is useful to note that the voltmeter reading on a closed circuit of 10 ohms gives the current flowing in milliamperes by moving the decimal point to the right, thus, in the above circuit when the voltmeter read 1.12 volts, 112 ma were flowing, therefore the use of an ammeter is superfluous. Should such an ammeter be used its resistance must be deducted from the standard 10 ohm coil used, or else the resistance plus the resistance of the meter will be in excess of 10 ohms.

Another example—a wireless high-tension battery of 84 cells shows an E.M.F. of 131 volts on open circuit, and 129 volts P.D. on closed circuit through 12,600 ohms load resistance.

Then the total I.R.

$$= \frac{131 - 129}{129} \times 12,600 = 194 \text{ ohms approximately,}$$

that is, 2.31 ohms per cell

We have already drawn attention to the point that when measuring the E.M.F. of these tiny cells a very delicate voltmeter must be used.

It is even more necessary to use a delicate instrument when taking the P.D., as the resistance of the instrument will lower the resistance of the load by acting as a shunt,

therefore, for accurate work, the resistance of the voltmeter in shunt with the loading resistance must be arranged when in parallel to work out at 150 ohms per cell.

Looked at from another point of view, the battery in question will be giving approximately 10 ma. through a load of 12,600 ohms.

Suppose our voltmeter is a good one and takes only 2 ma for a full deflection of 130 volts, then at the moment of taking the reading the cells will be giving $10 + 2$ or 12 ma, that is, an overload which makes for inaccuracy.

CONSTANT CURRENT TEST. Another method of testing cells is to place them on a load of variable resistance and to keep the current constant; thus, a large cell may be set to give 2 amp discharge, and the E M F and P.D noted daily. As the P D falls, resistance is cut out to keep the current constant. Such a method is very suitable for cells intended to work glow-lamps and valves, and is also applied to high-tension wireless batteries, the current being set at 5, 10, or 15 ma, according to the size of the battery.

The above tests give a very good idea of the ampere-hour capacity of the cells tested, but another question arises, that is, how will the cell behave when used intermittently over an extended period?

INTERMITTENT CIRCUIT TEST The Post Office test is to close the circuit for 5 hours a day per week, that is, 4 hours 17 minutes per day, including Sundays, or 30 hours a week in all. During this time the voltage on open and closed circuit is taken at a constant current of from 20 to 100 ma.

As the work the cell has to perform is now extended over a reasonably long period, any defect, such as heavy local action, becomes apparent. This test is really a short **SHELF TEST**. By a shelf test we understand a test in which the cells to be tested are put by and remain untouched for periods of 6, 12, or even 18 months or more without being called upon to pass any current.

Their E M.F is taken occasionally, and at selected times

one or more of a batch are put on the usual 10-ohm test to find out how much they have deteriorated during the period of storage. This test is, of course, more applicable to dry cells, which are made up and sold complete with the necessary paste electrolyte. It becomes necessary because of the delay which may ensue between the date of manufacture and the time the customer may purchase the cell after it has been stored by the various factors and dealers through whose hands it first passes.

The testing of dry cells is not an easy matter. The usual way is to short-circuit the cell momentarily with an ammeter to see if it gives a good current, that is, anything from 5 to 25 amp. This, however, while demonstrating the low internal resistance of the cell, is no criterion of the lasting-power of the cell or its life on shelf test. We shall revert to this point later.

DEPOLARIZATION TEST There remains now the test for depolarization. The Post Office test is to shunt the cell for 10 minutes through 2 ohms, first noting its E.M.F. The E.M.F. is again read as soon as the circuit is opened at the termination of the 10 minutes test.

The differences in voltages expressed as a percentage must not be greater than 20 per cent for cells of about 2 pints, and smaller or greater than 15 per cent for cells of about 3 pints and over.

Watt-hour Efficiency.

In concluding this section it may not be out of place to draw the reader's attention to the watt-hour efficiency of the cell.

For a certain consumption of zinc a certain number of ampere hours of current may be expected. The electrochemical equivalent of zinc is .00033698, that is, that quantity of zinc in grammes will be used up by one ampere in one second. This is equivalent to 1.213 gm. consumed per ampere hour, or .04245 oz.

This amount of zinc must be used per ampere hour, whether it is used in a Lalande cell or a Leclanché or a bichromate

But whereas in the first cell this ampere hour will be generated at a working pressure of something like .65 volts, that of the Leclanché cell will be approximately 1 volt, and of the bichromate cell 1.6 volts, so that the higher the E.M.F. the cell will generate, the greater will be the watt hour output for exactly the same consumption of zinc

Hence, the desirability of choosing a cell of higher E.M.F., other things being equal. In the above figures loss of zinc by local action has not been reckoned, but, of course, this factor must be taken into account when comparing cells

Point of Exhaustion.

In these tests above outlined it is usual to assume the cell exhausted when the voltage (P.D.) has fallen to half its original value (E.M.F.), thus, a bichromate cell of 2 volts would be accounted exhausted when its P.D. has fallen to 1 volt, or a Leclanché cell having an E.M.F. of 1.5 volts is considered discharged when its P.D. on load has fallen to .75 volts. As such a considerable drop in many cases renders the battery unsuitable for practical use, the ampere hours of Leclanché type cells are sometimes reckoned on a basis of 9 volts being the termination or limit of useful life

The Post Office specifies the limit of exhaustion as being when the E.M.F. of the cell falls to .975 volt

It is obvious the lower limit is not so important when the cell is operating, say, a bell circuit, as when working a valve or glow-lamp in which the current must be kept up to a minimum value.

It is sometimes recommended that the user should have another cell or two in reserve, so that such cells can be placed in circuit as the main battery fails. The author does not recommend such a course, because, beside being a

makeshift, it is better to spend the cost of the reserve cells in buying a larger main battery. Further, when the main battery fails the reserve cells are left on the user's hands only partially discharged. This applies more emphatically to wireless high-tension dry cells.

Desirable Points in Cells.*

In choosing a cell we have naturally to bear in mind the particular class of work for which the cell is intended, but, generally speaking, the following points are desirable—

- 1 High E.M.F
- 2 Low I R.
3. Constancy
- 4 Small local action.
5. Cheapness.
6. Preferably be single fluid
7. Simplicity and absence of mess.
8. Ease of recharge.
9. Should be non-poisonous, odourless, and inoffensive.

The Choice of Cells.

For bell ringing, electric clock circuits, and general signalling, Leclanché cells are very suitable, also A D. cells. Of the Leclanché cells preference should be given to the sack type if first cost is not of paramount importance, as the porous pot type is more prone to fur up owing to the capillary attraction of the pot. Daniell cells have been much used for telegraph work, or on circuits that are almost continuously closed. For heavy continuous work, such as when charging accumulators, running small electro-motors, etc., when the work desired is of a few hours' duration only, the bichromate, either single or preferably double fluid, is practically essential.

If a heavy current is required intermittently, such as for

* *Electrical Review*, August, 1928, p. 223. "Primary Wet Cells." A. M. Codd.

operating railway track and signal circuits, or working small electro-motors, Lalande cells can be used. Owing to their low voltage, the necessity of handling caustic potash, and their expense, these cells are not commonly used in this country. In America, however, owing to their low freezing point, they find a certain amount of favour for railway work.

For working electric glow-lamps or wireless valves, that is, for giving a fairly heavy current intermittently, say, for some hours daily, Lalande cells can be used, also large A D. and Leclanché elements will do the work, but batteries of the ferric chloride type keep a more constant P.D. and, owing to their absence of recovery, with a momentary and fictitious rise in voltage overnight, are unlikely to burn out the filaments, as sometimes happens with Leclanché batteries in use.

For wireless high-tension batteries, where portability is not the first essential, wet A D. or Leclanché cells should be used in preference to the dry form, as they are more to be relied upon in all cases.

On the other hand, batteries for medical purposes, ionization, testing sets, etc., necessitate almost always the use of dry batteries for portability.

In concluding this section there is one method of obtaining relatively heavy currents intermittently which is generally overlooked. Of course, we can charge an accumulator directly by means of a bichromate or other suitable cell, and have done, but a better method consists in trickle charging the accumulator cell or cells by feeble currents continuously applied by A D., ferric chloride, or Daniell cells. In particular, the Daniell cell shows up well on the score of cost, and, as the circuit is always closed, some of the disadvantages of this cell are minimized, particularly if the gravity form is used. Owing to the rise in P.D. of the accumulator cell when charged the arrangement is almost self-governing.

The accumulator used for this purpose when first set up should be nearly fully charged, particularly when air depolarizing cells are used, as otherwise a larger rush of charging current will initially be required of a greater strength than the cells can economically furnish.

CHAPTER III

PRACTICAL CELLS

IN describing some of the more useful cells to-day in use we propose to give approximate data of each cell's performance, as hitherto the actual output of any cell of given cubic capacity has, with few exceptions, been given extremely indefinitely

A Standard Cell.

For purposes of comparison between cells of different types, the author has used a Standard cell containing roughly one quart when brim full. The porous pot itself when used as a two-fluid cell holds about half a pint, and when stood in the outer container, together with the necessary carbon electrodes, limits the contents of the outer cell to one pint

In the following experiments, therefore, we have the outer cell containing the depolarizer holding an exact measured one pint, and the inner porous pot holding, roughly, half a pint of excitant

As a single-fluid cell, the container in each experiment has had its contents measured to a total of $1\frac{1}{2}$ pints only, exclusive of the electrodes.

Single-fluid Cells.

AIR DEPOLARIZING CELLS Probably the simplest of all cells are those that derive their depolarizing properties from the oxygen of the air

We have already seen that Maïche made early attempts on these lines with some little success For light work, indeed, such as the occasional ringing of bells in a small house, a single zinc-sal-ammoniac-carbon element, having

relatively large carbons as in the Law cell, is quite adequate. From one point of view it is good practice to fit such a cell with a close-fitting lid to prevent evaporation of the sal-ammoniac solution, since evaporation is one of the chief defects of such cells, as it leads to crystallization and consequent creeping of the solution up the walls of the container and also frequently up the electrodes. In the case, however, of true air depolarizing cells, we cannot use a lid, since to do so would cut off the supply of air on which the



FIG 6 AN A.D. (AIR DEPOLARIZING) CELL
(Messrs. Le Carbone)

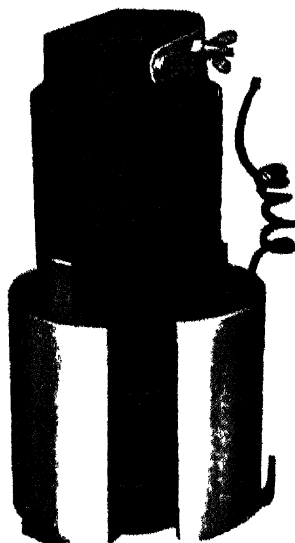


FIG 7 COMPONENTS OF THE
A.D. CELL

recovery of the cell depends, so such cells must be left open and preferably in a well-ventilated position.

THE A.D. CELL (Messrs. Le Carbone) It will be seen (Fig. 6) that this cell consists of an outer container holding the sal-ammoniac solution in which stands a totally-immersed zinc cylinder and, concentrically within it, a tall cylinder or block of porous carbon only about half immersed and separated from the zinc cylinder by rubber bands. Contact is established with the zinc by means of insulated

flexible wire soldered to the bottom of the zinc cylinder (Fig 7)

The charge of excitant is about half a pound of sal-ammoniac per pint of water. As this is too much to be effectively dissolved and forms a saturated solution, the surplus salt drops to the bottom of the cell and is used up gradually as the life of the cell progresses. When the circuit is closed the main action is as follows—



that is, the ammonium chloride (sal-ammoniac) attacks the zinc to form zinc chloride with the evolution of the gases of ammonia and hydrogen

The hydrogen would tend to polarize the cell in the usual manner were it not for the special depolarizing property of the carbon

As we have mentioned, this carbon is of a porous nature, so that it is able to occlude or breathe in abundantly of the oxygen of the air. However, were it ordinary porous carbon, naturally the part immersed would quickly become saturated with the solution in which it is partially standing, but the special feature of the A D carbon is the process of rendering it water-tight by means of a colloidal film, which enables a good contact to be made between the carbon and the electrolyte and yet maintains the interior of the carbon dry, so that the gases may circulate and combine with the occluded oxygen of the air. Of course, should the special carbon from any defect become waterlogged, the cell will cease to act satisfactorily

The actual amount of salt consumed by a cell of this description is theoretically about 2 grm. per ampere hour, and the makers claim this figure to be well adhered to

The hydrogen, having combined with the atmospheric oxygen at the surface of the depolarizing carbon, is returned to the cell as water, nevertheless, it is necessary from time to time to add water to make up the losses due to evaporation

The formation of crystals shows the solution to be too weak. Occasionally, under heavy discharge, a crust is formed in which the gases will collect, thereby raising the level of the electrolyte. Under such circumstances this crust must be broken by gently rocking the carbon, so that

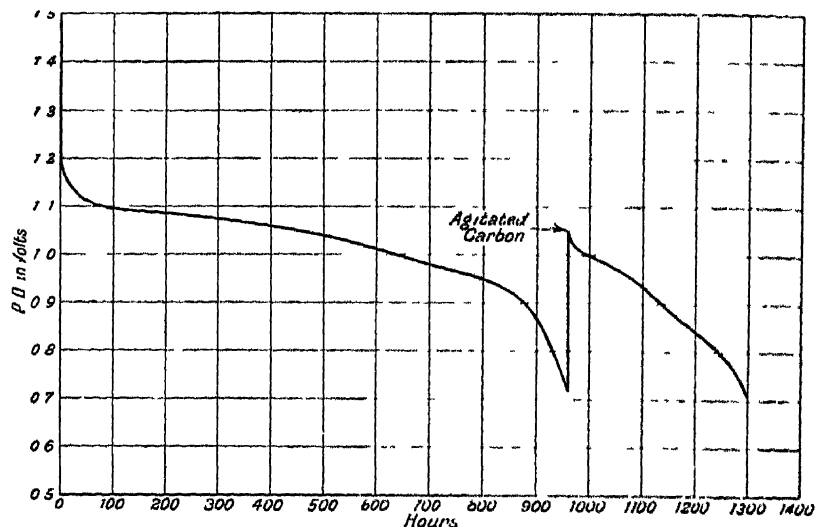


FIG. 8 CURVE OF DISCHARGE OF A D 2-PINT CELL (No. 240) THROUGH 10 OHMS

the gases may escape from the pockets in which they have collected.

Fig. 8 shows a curve of discharge taken by the writer for a No. 240 quart-size cell, holding about 1 pint of concentrated electrolyte.

The extreme constancy will be noticed in conjunction with the high ampere-hour capacity— in this case well over the 100 ampere hours claimed by the makers, despite the fact that the cell was, by discharging through 10 ohms continuously, passing a current about double that imposed by the manufacturers, i.e. 50 ma.

It should be realized that though the zinc is used up

at the end of the discharge of the cell, the carbon electrode is good for at least three lives without appreciable deterioration

To allow of larger current discharges the A D cell is made also with two large carbon units in a single cell. This cell having an I.R. of approximately 0.25 ohm can give frequent momentary discharges of 10 amp, 2 amp for short periods, or 1 amp for 8 hours a day

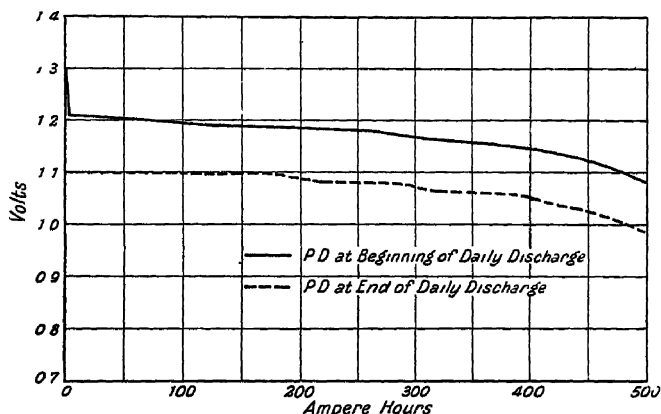


FIG 9 CURVE OF DISCHARGE OF A D CELL No. 222
(LE CARBONE)

Fig 9 shows the curve of discharge supplied by the makers of this cell, size $9\frac{3}{4}$ in \times $7\frac{7}{8}$ in \times $6\frac{1}{2}$ in, when giving 1 amp for 4 hours daily, the total capacity being 500 ampere hours

These cells can also be used in a caustic soda electrolyte in special cases if desired

THE FÉRY CELL (Fig 10) is also an air depolarizing cell, the carbon being specially shaped as can be seen from the illustration, and only semi-submerged in the sal-ammoniac solution

The zinc is a circular collar, or else a plain flat plate placed at the bottom of the cell

When the circuit is closed the chloride of zinc formed falls to the bottom of the cell, thereby covering the zinc, while the carbon continues to work in clear sal-ammoniac solution which is itself, to a certain extent, oxygenated by the air.

As 992 cub. cm of air contain about 208 cub. cm of oxygen, the importance of good ventilation, so that the air

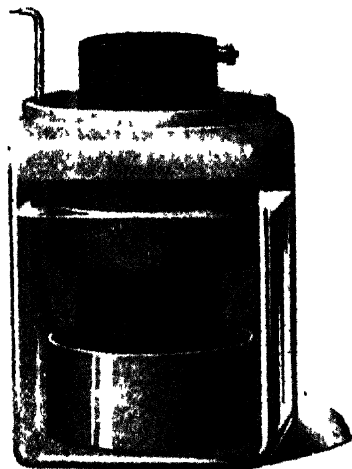


FIG. 10. FÉRY AIR DEPOLARIZING CELL.

is free to circulate about the exposed extremities of the carbon electrodes of air depolarizing cells, is manifest. Cells of this type are very economical in zinc consumption, the theoretical figure being closely attained.

The output from these cells being relatively rather feeble compared to some other cells of different make, the manufacturers advise their use in charging secondary cells if heavy currents are needed. They advise accumulator cells of a capacity of about 10 amp.-hr., so that the losses in the accumulator (being small) will not play a preponderating

part, losses which would again otherwise have to be made up by the primary charging cells

Fig 11 shows a curve of discharge for a Féry cell at 14 ma. extending over a period of more than 300 days, the total capacity claimed being 105 amp.-hr for what would roughly be a quart cell.

It should be noticed that air depolarizing carbons should

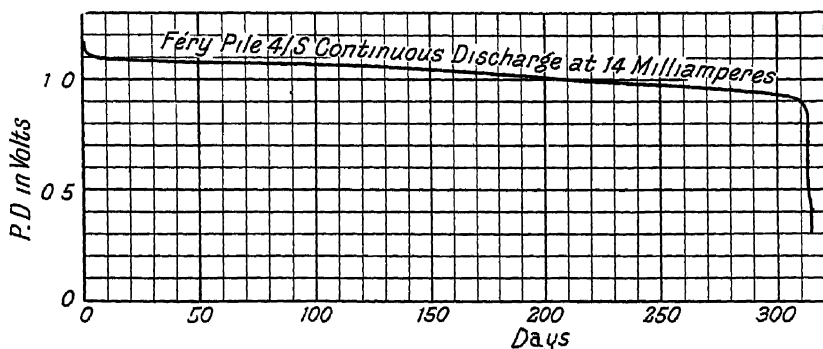


FIG 11 DISCHARGE CURVE OF FÉRY CELL $5\frac{1}{2}$ IN \times $4\frac{1}{2}$ IN \times $4\frac{1}{2}$ IN AT 14 MILLIAMPERES CONSTANT

not be washed, it is sufficient to scrape them clear from any adhering crystals, etc, with a piece of blunt wood

Chemical Depolarizers.

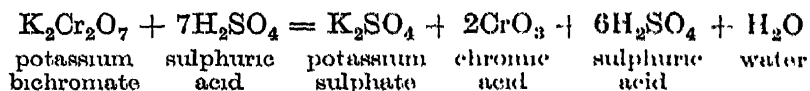
THE BICHROMATE CELL appears to have been first suggested by Poggendorff, and in its usual form consists of a zinc plate sandwiched between two plates of carbon, the whole immersed in a solution of chromic acid or bichromate of potash or soda mixed with dilute sulphuric acid. Numerous modifications of this arrangement have been suggested to which the inventors have attached their names, the most common being the Grenet, a bottle-form of cell in which the zinc is screwed on a brass rod free to slide up or down, so that the zinc plate can be immersed

in the solution or withdrawn at will from outside the bottle. This form suffers from the disadvantage that the brass rod and its rubbing contacts soon corrode and fail to effect good contact.

Probably the best form is that ascribed to Trouvé, in which a small windlass with cords raises both the elements complete from the solution, the zinc and carbon being attached to a wooden crossbar. A modified form is shown in Fig 45.

The active depolarizer is chromium trioxide, CrO_3 , which may be used itself, or, as is more commonly the case, by acting on potassium bichromate or soda with sulphuric acid

Thus



that is, when the acid is added to potassium bichromate, potassium sulphate and chromic acid are formed.

As soon as the acid in the solution attacks the zinc we have the evolution of hydrogen which would tend to polarize the carbon, but the hydrogen is seized by the oxygen in the chromic acid forming water and chromium sesquioxide.

Various combinations of salts have from time to time appeared, but that given by Professor Ayrton seems as good as any and has been adhered to by the author in the following experiments. The solution is prepared as follows. Add 1 lb. of potassium bichromate crushed to $9\frac{1}{2}$ pints of cold water, and pour in, slowly, 1 pint of sulphuric acid (S.G. 1.840). Reduced to smaller quantities this equals, roughly, 27 fl. oz. of water, 3 fl. oz. of sulphuric acid, and $2\frac{1}{2}$ oz. of potassium bichromate, forming in all about $1\frac{1}{2}$ pints of solution. The water alone may not dissolve the potassium bichromate, but on adding the sulphuric

acid to the mixture the warmth generated will effect solution. One-seventh of the oxygen in the potassium bichromate is used to form water, and one part of the sulphuric acid is used to form potassium sulphate. Three more parts of the sulphuric acid are used to form chromium sulphate,

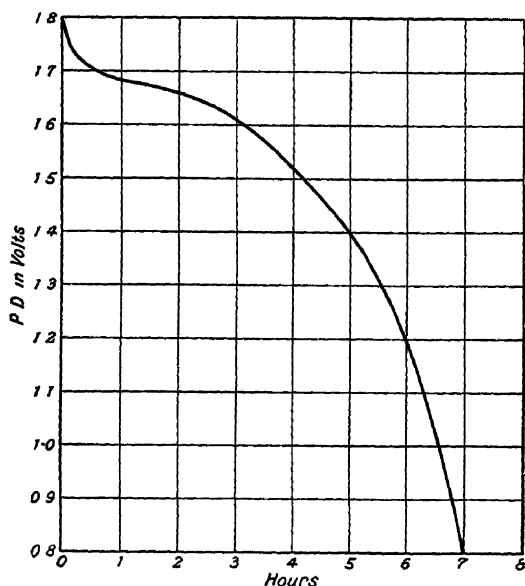


FIG 12 CURVE OF DISCHARGE AT 1 AMP OF
1½ PINT SINGLE FLUID BICHROMATE CELL

leaving still three parts of acid to attack the zinc and form zinc sulphate. The proportion of sulphuric acid given can be raised a little if desired, without harmful effects. This solution was used in our Standard cell in conjunction with one zinc (amalgamated) and two carbons 2 in wide immersed for a depth of $4\frac{1}{2}$ in. The distance between the zinc and carbons on each side was $\frac{1}{4}$ in. Total zinc area = 18 sq in, current on short circuit fresh = 13 amp. Fig 12 gives the curve of P.D. on a constant discharge of 1 amp.

Thus we see the total ampere hours are under 7 at an average P.D. of roughly 1.4 volts, reckoning the cell exhausted at .8 volt. The I.R. of the cell equals .26 ohm approximately

Single-fluid bichromate cells are not very economical, nor can they be left on open circuit. Unless extremely heavy currents of short duration are required, the double-fluid form (described in that section) is much preferable.

Potassium bichromate cells are apt, particularly when nearing exhaustion, to form crystals of chrome alum, which are not easy to dislodge

On this account, and also because of its superior solubility, sodium bichromate is frequently recommended. Sodium bichromate is also relatively cheaper, but contains more water of crystallization, so that about twice the weight must be used, but on the whole sodium bichromate is the better salt.

As the active principle of depolarization is chromium trioxide, chromic acid itself can be used with advantage, and is probably superior to either sodium or potassium bichromate.

In the previous formula it suffices to substitute about $1\frac{1}{2}$ oz. of chromic acid for the potassium bichromate, using 27 fl. oz. of water and 3 fl. oz. of sulphuric acid as before

Potassium permanganate has been suggested as a substitute for potassium bichromate, but, although it gives a higher initial voltage, the current drops much more suddenly

It is also difficult to dissolve, and forms an unpleasant slime upon the electrodes; altogether, it is not to be recommended.

Various patents have been taken out for ready prepared chromium salts; thus, Voisins red salt is prepared by dissolving sodium sulphate in sulphuric acid and adding the potassium bichromate. This is allowed to set and stored in bottles. Probably the simplest storable mixture is that

suggested by Dronier, in which 1 part of potassium bichromate is mixed with 2 parts of potassium bisulphate, 3 parts of this mixture being added to 20 parts of hot water.

FERRIC CHLORIDE CELLS. Figuer, in 1863, appears to have been the first to use a mixture of concentrated ferric

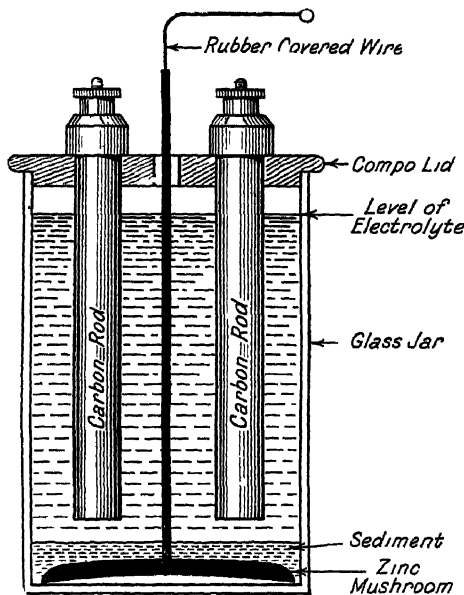


FIG 13 DIAGRAM OF CODD CELL

chloride and sulphate as a single-fluid cell with electrodes of zinc and carbon (E M F 1.5 volts)

Such an arrangement gives excellent results, but, unfortunately, the zinc is strongly attacked, so that the cell cannot be used for open-circuit work. Actually, the addition of the ferric sulphate appears to be of no advantage, and ferric chloride alone gives better results. The advantage of ferric chloride over other depolarizers is its extreme constancy, which persists until the solution is almost exhausted, also it is very soluble and, if properly used,

leaves the cell and electrodes in a clean condition with an entire absence of hard crystalline deposit; moreover, it is one of the cheapest depolarizers procurable

Pabst, later, in 1884, endeavoured to overcome the difficulty of the susceptibility of zinc to attack by substituting a block of iron, but with a drop in voltage to $\cdot 78$ volt

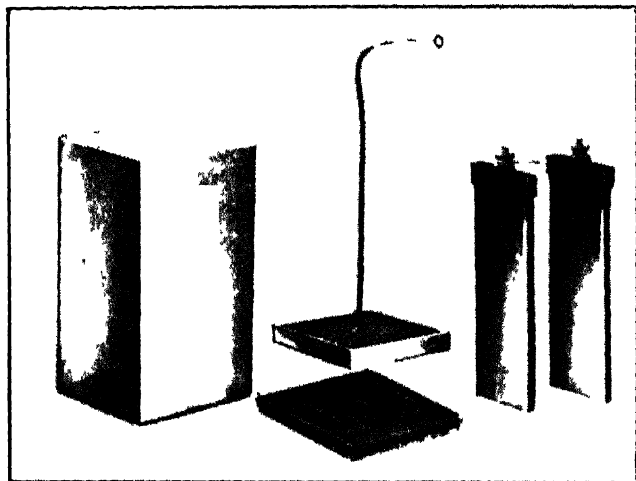


FIG. 14 Codd CELL TAKEN APART

The iron, too, is still attacked, although more slowly than zinc, so that on open circuit the ferric chloride becomes reduced with formation of objectionable iron rust deposit

Since then all the attempts to use ferric chloride seem to have been made on the lines of two-fluid cells, which will be enumerated in the appropriate section.

The author has, however, successfully used ferric chloride in a single-fluid cell of special design, as follows—

Codd CELL This cell consists of a container, at the bottom of which is arranged a close-fitting flat zinc plate. Connection from the plate to the exterior circuit is made through a rubber-covered wire. The container is fitted

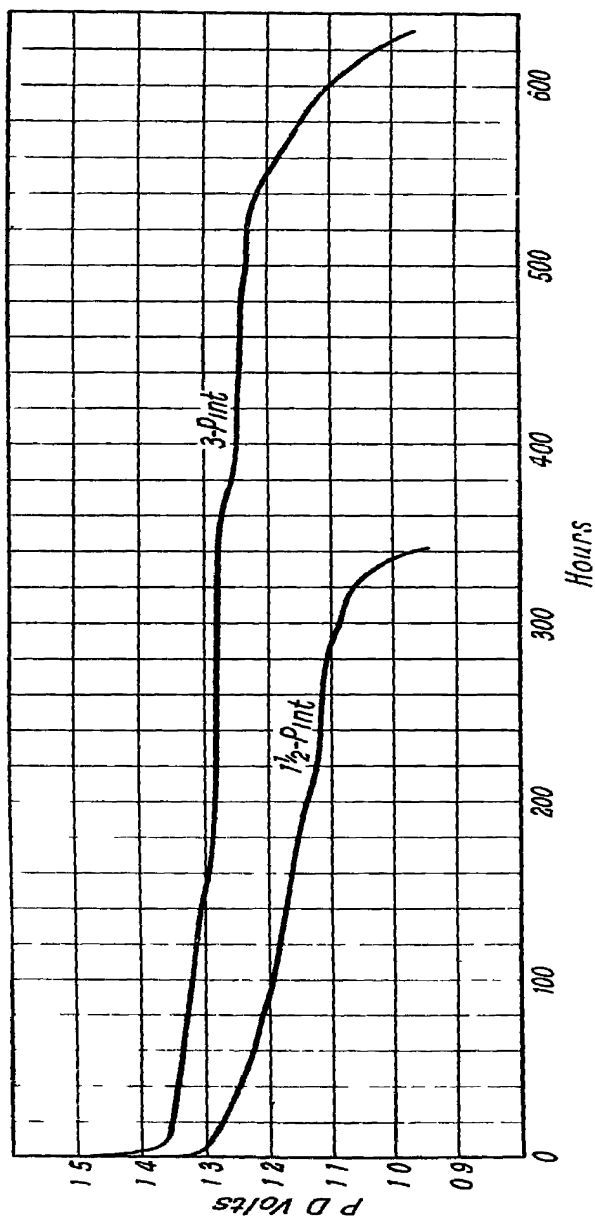


FIG 15, CURVES OF DISCHARGE OF $1\frac{1}{2}$ AND 3 PINT CODD CELLS ON 10 OHMS

with a lid from which hang one or more carbon plates (Fig. 13), reaching to within about $\frac{1}{2}$ in. of the zinc plate. A little mercury is placed on the zinc plate to keep it amalgamated, and the cell filled with a solution of ferric chloride containing a little sand or the like in suspension. As soon as the cell is at rest the sand settles over the zinc at the bottom, and in covering it serves the purpose of a mobile porous pot. Fig. 14 shows the simplicity of the cell taken apart.

Such a cell has an E.M.F. of 1.52 volts, and gives a remarkably constant and high P.D. till the end of its life, when it rapidly falls off and the cell is exhausted. Thus, the current is given at a useful pressure during the whole of the life of the cell, and the watt hours in consequence are high, in fact, higher in relation to the ampere-hour capacity than with any other known cell. Fig. 15 gives curves of discharge for cells of two sizes through 10 ohms resistance.

A cell holding $1\frac{1}{2}$ pints of solution has an I.R. of about .6 ohm, depending on the amount of sand present and the nearness of the electrodes one to another.

The capacity of the cell is about 24 amp.-hr. per pint of normal solution, or about 29 watt-hours, at a mean voltage of 1.2 on closed circuit at a reasonable output. Local action on open circuit is small, and zinc consumption appears to be in the neighbourhood of 1.3 gm. per ampere-hour.

The action of the cell seems to be the following. The ferric chloride attacks the zinc, forming zinc chloride which, being of a greater density than the ferric chloride, lies at the bottom of the cell and protects the zinc plate, a clear zone being distinctly visible after the cell has been in use some time. The function of the sand is to form a refuge for the zinc chloride to prevent its being disturbed by convection currents in the ferric chloride on long periods of open circuit. For short periods up to, say, a fortnight, if the cell is exhausted quickly, the layer of sand may be

dispensed with, causing a consequent lowering of the I.R. of the cell. As the cell approaches the end of its life the clear zone expands, the ferric chloride becoming reduced and assuming a watery yellowish colour. At this point the cell can readily be cleaned by rinsing it under the tap, and recharged with ferric chloride, as the zinc is sufficiently robust to last out several charges of ferric chloride.

As the capacity of the cell in ampere-hours depends on the volume of its contents, the cells are usually made square or rectangular to economize shelf space (Fig 16), and also for convenience in the packing. These cells are capable of giving considerable currents for long periods; thus, a 3-pint cell will give $\frac{1}{4}$ amp for 300 hours continuously, or double that or more for periods of 4 to 5 hours daily at an average P.D. of about 1.2 volts. For ordinary purposes the

cell is deemed exhausted when it falls to a P.D. of 1 volt. Such cells work small glow-lamps, wireless valve filaments, etc., entirely satisfactorily, as well as furnishing weaker currents for open-circuit work, such as electric clocks, bells, etc., and are very cheap and easy to maintain.

MISCELLANEOUS CELLS To conclude this section, some allusion must be made to the cells devised by Marié Davy, Schanschieff, and De la Rue.

In the Marié Davy cell the elements are disposed in a horizontal direction, the carbon plate lying at the bottom of the cell, which is trough-like in shape. Above the carbon is placed a similar size plate of zinc, the space between

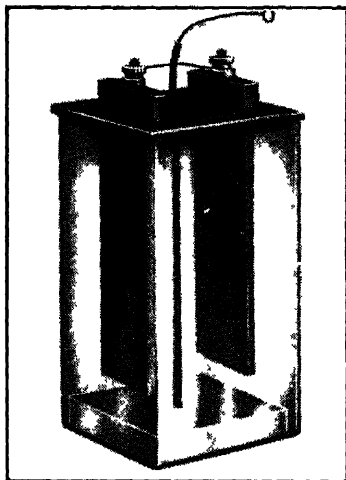


FIG. 16 CODD CELL
COMPLETE

them being filled with mercurous sulphate and the cell filled with water. The action is as follows. the zinc combines with the sulphuric acid contained in the mercurous sulphate, forming zinc sulphate and freeing metallic mercury. Some of this mercury goes to amalgamate the zinc plate, the rest falls to the bottom of the cell. Marié Davy also constructed a two-fluid form of this cell, the carbon with its mercurous sulphate being in the outer vessel, and the zinc within the porous pot in a dilute acid solution. The E.M.F. of these cells is about 1.5 volts, but they are rather feeble in action.

Schanschieff modified this cell by arranging the electrodes as a single-fluid cell in the orthodox position, using a zinc plate between two carbons, and also by using a specially-prepared mercury salt made by repeatedly dissolving metallic mercury in boiling sulphuric acid, the resulting salt being apparently a special acid form of mercuric sulphate. Very fair results can be obtained by using ordinary mercuric sulphate dissolved in sodium bisulphate or other suitable vehicles.

The cell is very clean to use, but in the writer's experience metallic mercury is liable to be deposited on the zinc, even on open circuit, so that the cell soon exhausts itself. Mercury salts are also very poisonous, and their high price renders the cell commercially out of court.

Cells similar to the above, but constructed with special precautions as to the disposition and purity of the materials employed, form the basis of the standard cells of Clark, Rayleigh, Carhart, and others.

The cell devised by De la Rue consists of a mixture of silver chloride, AgCl , fused round a central silver wire, the anode being zinc and the excitant a solution of salt (NaCl). Briefly, the salt acts on the zinc when the circuit is closed, forming zinc chloride, the hydrogen freed combines with the chlorine in the silver chloride to form hydrochloric acid, and silver is deposited on the silver cathode.

Ammonium chloride was later substituted for salt, the E M F of the cell being about 1.04 volt

These cells are somewhat feeble and, of course, expensive, but it will be remembered it was with a battery of over 14,000 of such cells that De la Rue performed the first experiments in spark discharge in air and in vacuo, and they are of interest as illustrating a system of depolarization.

CHAPTER IV

SINGLE-FLUID CELLS WITH SOLID DEPOLARIZERS

UNDER this classification we have two of the most important cells in practical use to-day, viz., the Lalande and the Leclanché

THE LALANDE CELL, as first devised, consisted of a vessel at the bottom of which was a copper or iron cup containing copper oxide. A wire riveted to the cup leads upward to the outer circuit (Fig. 17).

At the top of the vessel was suspended a zinc ring or plate, which constituted the negative pole. The cell was filled with a solution of caustic potash or soda, about 1 lb. of caustic soda being dissolved in 4 pints of water

When the circuit is closed the zinc is attacked and sodium zincate formed, while the hydrogen generated reduces the copper oxide to metallic copper, the sodium zincate remaining in solution.

There is practically no local action whatever with this cell on open circuit.

The chief disadvantages of these cells, apart from expense, are the low E.M.F. generated, which rarely exceeds .75 volt, and the necessity of using caustic soda. In order to avoid the solution being converted into carbonate, a film of oil is generally floated over the caustic soda, in itself rather a messy operation, especially on recharging the cells. In some forms of this cell oil is incorporated with the granulated copper oxide. When the caustic soda is first mixed with water, sufficient heat is generated to throw out the oil, which then floats on the surface of the solution.

On the other hand, this cell is extraordinarily constant,

and can be made to furnish really powerful currents. In one form of this cell the iron cup is enlarged so as to form not only the electrode, but the container as well. With our Standard cell an iron tray, $3\frac{1}{2}$ in. in diameter and $\frac{3}{4}$ in. deep, was arranged at the bottom of a glass vessel, the usual

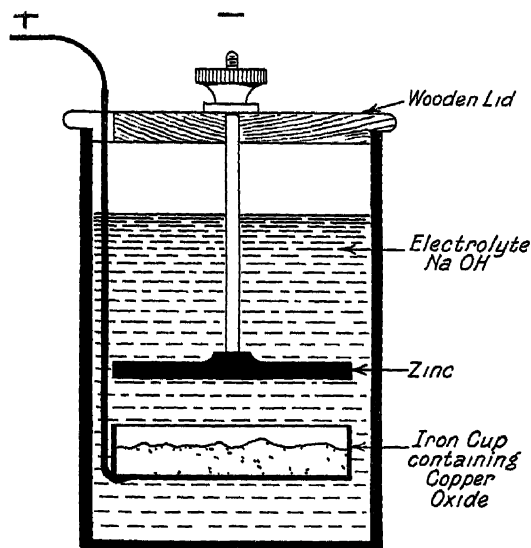


FIG 17 DIAGRAM OF LALANDE CELL

conducting wire running up the side and being insulated with rubber. Eight ounces of granulated copper oxide were emptied loosely into the tray. A zinc plate, about $3\frac{1}{2}$ in. in diameter, was suspended from the lid about 1 in. from the bottom of the tray, and the cell filled with about 1 pint of soda solution. The original E.M.F. was about .76 volt, and the cell gave 2.5 amp on short circuit, the I.R. averaging about .5 ohm.

Fig 18A shows the curve of discharge through 10 ohms. This gives roughly 130 amp-hr per pound of copper oxide, but the watt-hours output handicaps its performance,

because, roughly, twice as many Lalande cells must be used for a given voltage as other ordinary cells

When discharged at the higher rate of .5 amp. continuously (Fig. 18B), the performance in ampere hours is not so

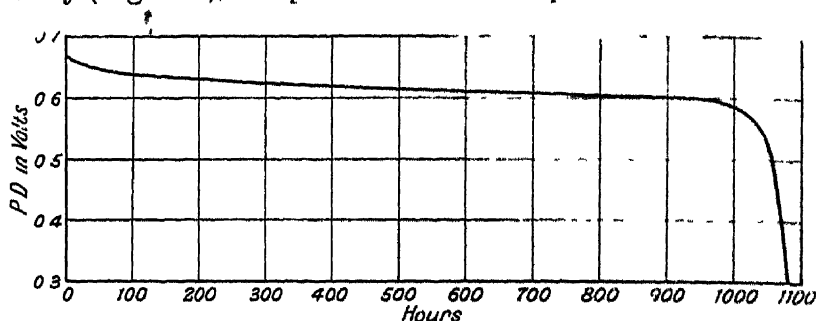


FIG 18A. CURVE OF DISCHARGE OF LALANDE CELL ON 10 OHMS

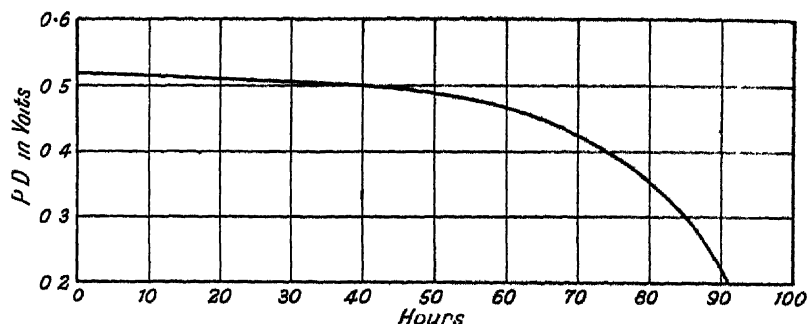


FIG. 18B CURVE OF DISCHARGE OF LALANDE CELL AT .5 AMPERE

good, but a continuous steady current of $\frac{1}{2}$ amp. can be relied on for 50 to 60 hours. The more modern form of Lalande cell (Fig. 19) has the copper oxide compressed into plates clamped in copper frames, and suspended from the lid of the cell, from which also hang the zinc plates, usually one on either side and amalgamated. These zinc plates are frequently cast with a depression at the bottom, this depression naturally being the first part of the plate to

dissolve away into a hole, thus furnishing ocular warning that the cell is nearing exhaustion.

These cells are arranged in deep glass jars, so that the sodium zincate tends to fall to the bottom, leaving the body of the electrolyte uncontaminated. Oil is floated on

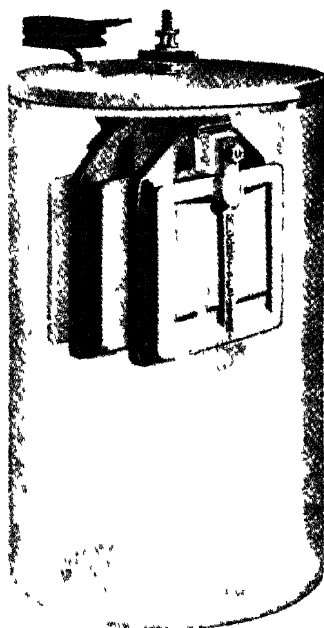


FIG 19 MODERN LALANDE CELL

the surface of the liquid to avoid its carbonating. Such a cell, about 13 in deep by $6\frac{1}{2}$ in diameter, will furnish 500 amp-hr, the working voltage being about 65 volts

THE LECLANCHÉ CELL, to-day, is the most widely-used cell in existence, quite apart from that form of Leclanché cell with immobilized fluid, usually called the "dry" cell. Owing to detail improvements, it has gradually superseded

other forms of cell, except for special purposes, doubtless owing to its capability of remaining inert and, with little local action, over long periods of, say, one or two years, with a minimum of attention. As we shall see from output

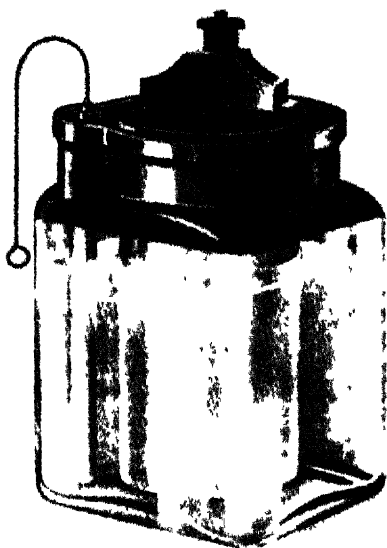


FIG. 20. LECLANCHÉ CELL.
(POROUS POT FORM)

tests, the original feeble currents have been greatly augmented by development of the components of the cell, and, while on a constant current basis it cannot compete with the bichromate, ferric chloride, and other forms of primary cells, yet its relative freedom from diseases and ease of installation render it very popular. To De la Rue is usually ascribed the suggestion of using manganese dioxide as a depolarizer, but the credit of working out the details of the cell and making it a practical success belongs to

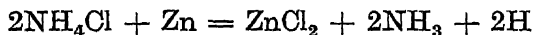
Leclanché, who first introduced the cell in 1868. Countless different forms have been invented, but the essentials remain to-day very much the same as when it was first devised, the main improvements being in the care and selection of the ingredients used in preparing the depolarizing material. On this account we shall only describe a few of the best known and more useful forms of Leclanché cell.

The original Leclanché cell (Fig. 20) consisted of a square glass jar with a neck in which a lip is formed to accommodate the zinc electrode in the form of a rod. Within the neck is placed the porous pot which contains the carbon plate, or rod, packed around with a mixture of crushed carbon and manganese dioxide. The porous pot is usually sealed with pitch, two small glass tubes being left protruding to act as vents for the gas generated.

The cell is charged with a solution of ammonium chloride, that is, sal-ammoniac, NH_4Cl .

Such cells give an E M F of 1.55 volts, which may rise to as high as 1.75 volts in cells charged with specially selected and prepared manganese, but for practical purposes the working E M F, after the first few hours, is 1.4 volts, the internal resistance of porous pot cells varying from 1.2 ohms in the pint size to .8 ohm in the 3-pint size with zinc rod electrode when the cells are new, but this resistance tends to increase as the cell ages.

The action of the cell is as follows. When the circuit is closed the zinc is attacked by the ammonium chloride, forming zinc chloride (which tends to fall to the bottom of the cell), free hydrogen and ammonia gases. Thus,



the hydrogen combines with the oxygen of the manganese dioxide, forming water and reducing the dioxide to manganese sesquioxide, thus



the escaping ammonia gas can usually be smelt when the cell is working heavily, and tends to corrode the brass terminal and lead caps of the carbon.

After a current has been passed for a few minutes the exposed surfaces of the manganese ore refuse further to effect depolarization, and the current falls off, but a further period of rest will enable the manganese to neutralize, as it were, its hydrogen opponent, and the cell will again recover. It is this slowness of solid depolarizers which is the chief disadvantage of cells using them, and we may here consider what steps have been taken to counter this disability.

Firstly, manganese dioxide alone cannot be used, for although when fresh it is a fair conductor, as the sesquioxide its resistance increases greatly, so it is necessary to add a certain amount of crushed carbon to ensure good conductivity.

In ordinary cells the proportion is about half and half, the poorer cells naturally having a larger proportion of carbon, the better class of cells having as much as 80 per cent of manganese in their composition, moreover, plum-bago or graphite is substituted, wholly or in part, for the crushed carbon, to gain in conductivity.

Secondly, the size of the granules of the mixture plays an important part. If the grains are large, the electrolyte can penetrate the mass with a consequent lowering of the resistance of the cell, but the depolarizing effect will be relatively short; on the other hand, if the grains are too fine, the depolarizing effect will be increased, but, owing to the closeness of the mass, the electrolyte will not be able readily to penetrate, and the object will again be defeated.

Thirdly, having determined the best mixture for the purpose for which the cell is intended, there remains the degree of tightness with which the ingredients shall be rammed into the pot; thus, if too tight, good conductivity will be ensured, but the electrolyte may not be able to penetrate,

also the pot may burst, if too loose, the contents of the pot may shake loose in transit and alter the quality of the cell

In order to bind the manganese-graphite contents, the powder is sometimes moistened with dilute hydrochloric acid or sal-ammoniac solution

It will, therefore, be seen that the charging of the pot of a Leclanché cell is largely a matter of experience.

The Post Office requirements in the fineness of the grain of the manganese ore are such that the powder shall pass through a sieve having 40 meshes to the inch, but shall be retained on a sieve of 60 meshes to the inch. Naturally, cells constructed to this high degree of quality are dearer than the cheaper forms usually sold for bell-ringing

The following table shows the approximate capacity that may be expected from a first-class porous pot cell, such as are supplied to the Post Office, large railway companies, etc —

		Capacity in ampere-hours to 75 volt	Porous pot size approx	I R. with rod zinc
No 1	3-pint size	60	$6\frac{1}{2}'' \times 3''$	8 ohm
„ 2	2 „ „	30	$5\frac{1}{2}'' \times 2\frac{1}{2}''$	9 „
„ 3	1 „ „	12	$4\frac{1}{2}'' \times 2''$	12 „

It must not be thought that such first-quality cells are readily accessible to the average user, and that they can be bought at any ironmonger's or electrician's shop

Fig 21 (a) shows the typical Leclanché discharge curve, taken by the author of a first-class cell of 2-pint capacity, and (b) an exactly similar cell purchased as high grade, such as would be suitable only for domestic bell-ringing purposes. The same electrolyte was used throughout in each test, had it been changed, as advised by the makers, slightly better results might have been obtained for curve

(a), but the writer considered that to change the electrolyte, when comparing with other types of cell, would be unfair.

The I R. of Leclanché cells falls a little if zinc cylinders are used. Thus, a No. 2 cell with cylinder instead of rod zinc would have an internal resistance of approximately

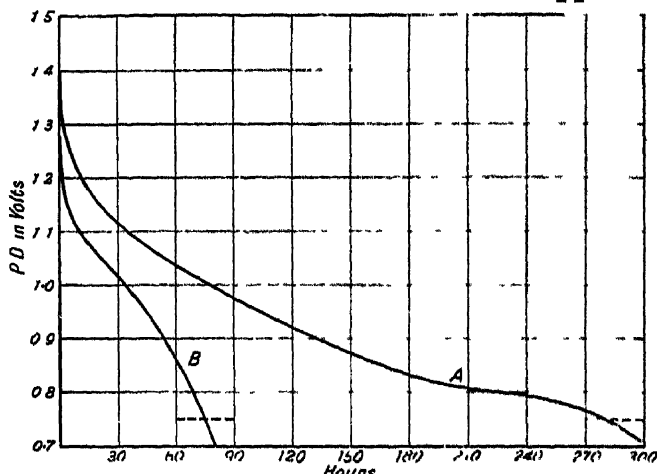


FIG. 21. CURVES OF DISCHARGE OF 2-PINT LECLANCHÉ POROUS POT CELLS ON 10 OHMS

(a) Special Quality (b) Commercial Quality

.5 ohm, but the greater portion of the resistance is created by the porous pot itself. Since the porous pot only fulfils the function of mechanically holding together the solid depolarizer, and not of separating two dissimilar fluids, means were sought whereby its use could be eliminated.

This can be accomplished in two ways, by using either agglomerate or sack cells.

The agglomerate cell (Fig. 22) depends in principle as before on the depolarizing action of the manganese carbon mixture, but this mixture, instead of being placed in the pot, is compressed with shellac or similar binding substance and moulded into porous blocks or rods.

Usually, two of these agglomerate blocks are placed one on either side of the flat carbon plate and kept in place by two india-rubber bands, a zinc rod or cylinder is placed in position completing the cell. Such cells are inferior to the porous pot form in capacity, but they are simple and have not much more than half the I R of a pot-type cell.

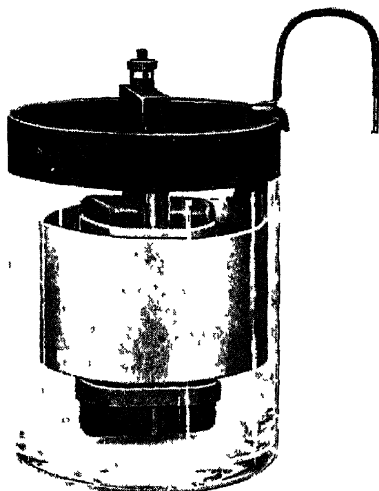


FIG. 22 AGGLOMERATE LECLANCHÉ CELL, SIEMENS
CYLINDRICAL TYPE

of similar size. A powerful form of this cell is the "6-block agglomerate."

In this arrangement, a circular central carbon rod, having 6 flutes moulded in its circumference, houses 6 agglomerate cylinders about 6 in. long of compressed manganese dioxide and carbon. The whole is wrapped in a turn of coarse canvas and kept in place by two rubber rings. Outside this is placed the zinc cylinder, the rubber rings and canvas preventing the electrodes from touching. Such a cell (Fig 23) has an internal resistance of only 25 ohm approximately.

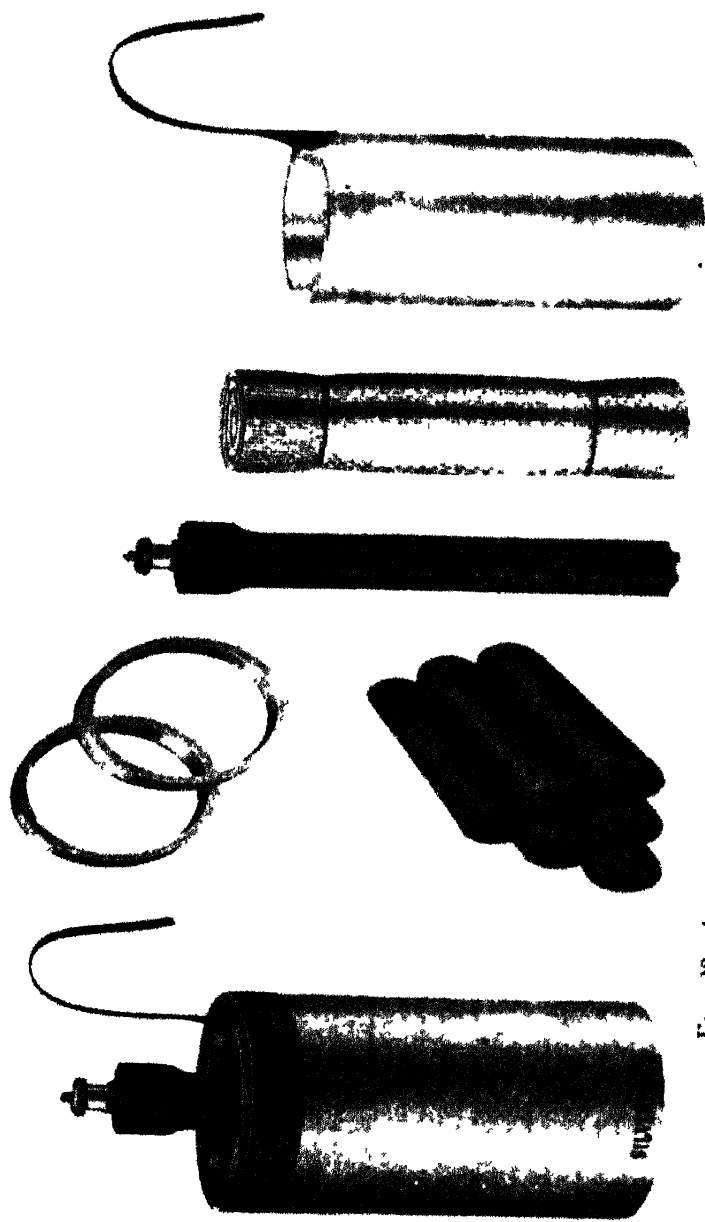


FIG. 23. AGGREGATE L'ÉCLAIRÉ (FILL SILVER) TYPE

Sometimes similar cells are used of twice the height, in which case two tiers of agglomerate rods are used—12 in all—when the resistance falls to about .15 ohm. Cells of this description are useful for purposes where sudden heavy currents are required, as in mining, or where a large number of bells, etc., are fitted, and can be sealed up for purposes of transport so as to avoid spilling the electrolyte and to reduce evaporation.

The last, or sack-type Leclanché cell is probably the



FIG 24 LECLANCHÉ SACK CELL SQUARE GLASS CONTAINER

most important, not only because it is in itself a very efficient form of cell, but because it is intimately connected, as we shall see in the appropriate section, with the manufacture of dry cells.

The sack form, as its name implies, consists of a cylindrical container of canvas or calico, which virtually forms a porous pot of negligible resistance, into which the powder of manganese and carbon is forced under pressure around the central carbon plate or rod. When the complete element comes out of the mould the sack is tightly wound

with several turns of twine to keep the contents tight, the bottom is treated with pitch and the top sealed in also, a cardboard ring usually serving as a guard for the compound.

Fig. 24 gives a good idea of the general appearance of a sack cell adapted to square glass container.

Such cells are very much more efficient than with the porous pot or the agglomerate form, since their capacity

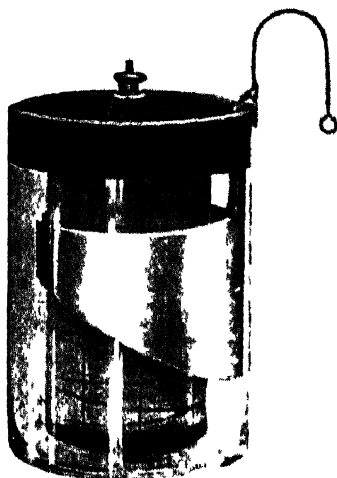


FIG 25. LECLANCHÉ SACK CELL CYLINDRICAL GLASS CONTAINER

is largely in excess of the former, while their I R. is as low or lower than the latter.

The superior capacity appears due to the fact that more pressure can be brought to bear in packing a sack cell than one using a porous pot, also the thinness of the sack enables a greater quantity of depolarizing mixture to be stored in the same space, while at the same time the internal resistance is greatly decreased.

As we have previously remarked, however, too much pressure must not be used in packing the sack in the

endeavour to obtain an ultra-high capacity, or the manganese mixture may become almost impermeable to the electrolyte. In any case, these highly-efficient sack cells are

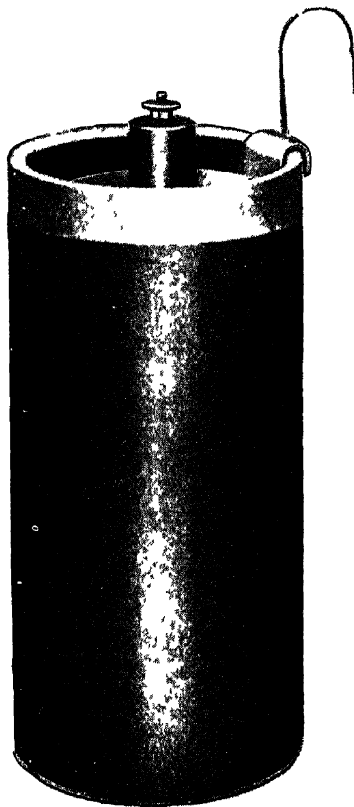


FIG. 26A LECLANCHÉ
SACK CELL, COMPLETE

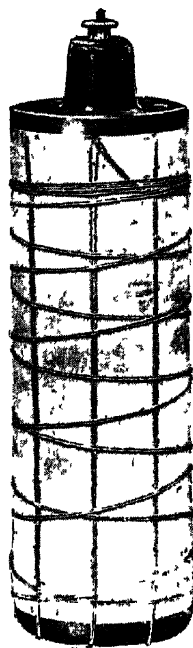


FIG 26B LECLANCHÉ
SACK ELEMENT

the better for at least 24 hours' soaking in solution before being put into use.

Sack cells are usually used with cylindrical or semi-cylindrical zincs, although zinc rods can be used if preferred at an increased I.R.

Approximate capacities for first-class sack elements are given as follows—

		Capacity in ampere-hours to 75 volts	Sack sizes approx	I.R. with zinc cylinder
No 1	3-pint size	110	6½" x 3"	25
" 2	2 " "	70	6" x 2½"	27
" 3	1 " "	30	4½" x 2"	30

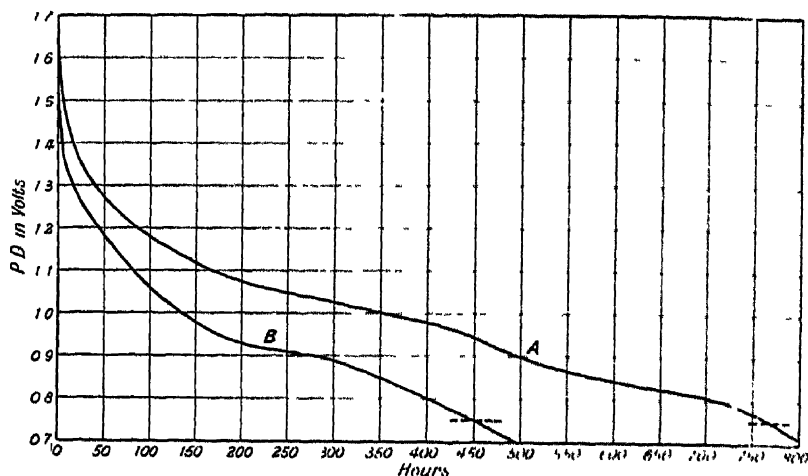


FIG. 27. CURVES OF DISCHARGE OF 2-PINT LECLANCHÉ SACK CELLS ON 10 OHMS

(a) Special Quality (b) Commercial Quality

Sometimes sack cells are put up in intermediate sizes, or in round glass jars, instead of the conventional square form. Fig. 25 illustrates the arrangement given to the cell by Messrs Siemens Bros., who also make a larger size sack than the No 1, known as the No 0 element. Two of these elements are sometimes used in two tiers united in the same sack, in which case the element is known as the No 00, illustrated in Fig. 26.

Fig. 27 (a) gives the curve of discharge taken by the

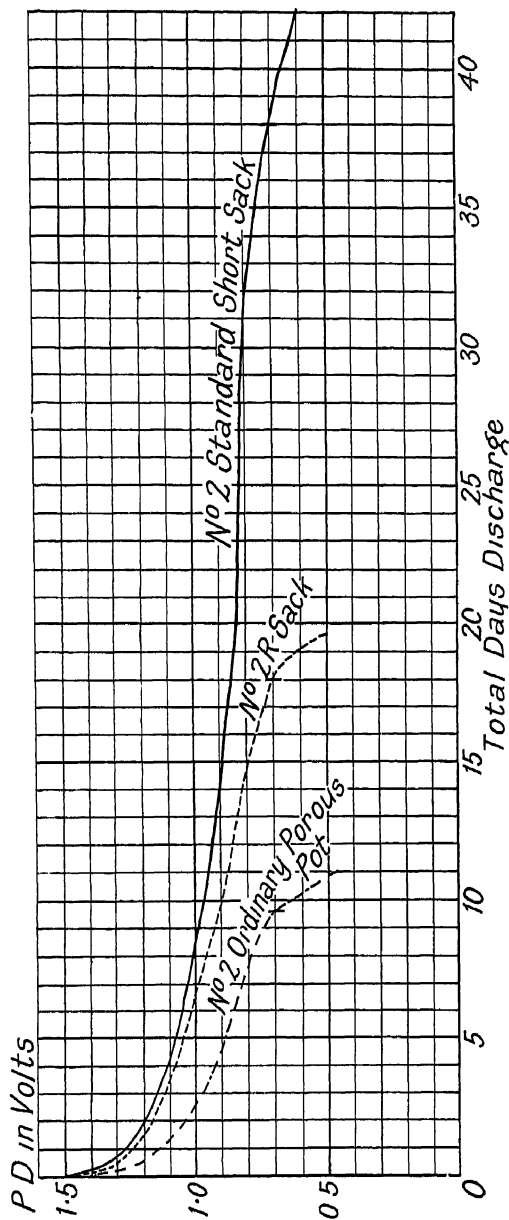


FIG 28 SIEMENS WET LECLANCHÉ CELLS THREE TYPES OF ELEMENTS FOR USE IN NO 2 SQUARE GLASS JARS ($3\frac{1}{2}$ IN SQUARE \times $6\frac{1}{2}$ IN HIGH, EXTERNAL DIMENSIONS)

External Dimensions		Average Output to 0.70 volt P.D.
No 2 Standard Short Sack Element	$2\frac{1}{2}$ in dia \times $5\frac{1}{2}$ in high (body) or $6\frac{1}{2}$ in high (overall)	80 amp -hours
No 2R Sack Element	$2\frac{1}{2}$ in dia \times $5\frac{1}{2}$ in high (body) or $6\frac{1}{2}$ in high (overall)	40 amp -hours
No 2 Ordinary Porous Pot	$2\frac{1}{2}$ in dia \times $5\frac{1}{2}$ in high (body) or $6\frac{1}{2}$ in high (overall)	20 amp -hours

The test curves are from average figures taken during *continuous discharges* through 10 ohms external resistance, using a 15 per cent solution of ammonium chloride. The cells were kept free from excessive crystallization by cleaning the zinc electrodes and renewing the electrolyte as considered necessary.

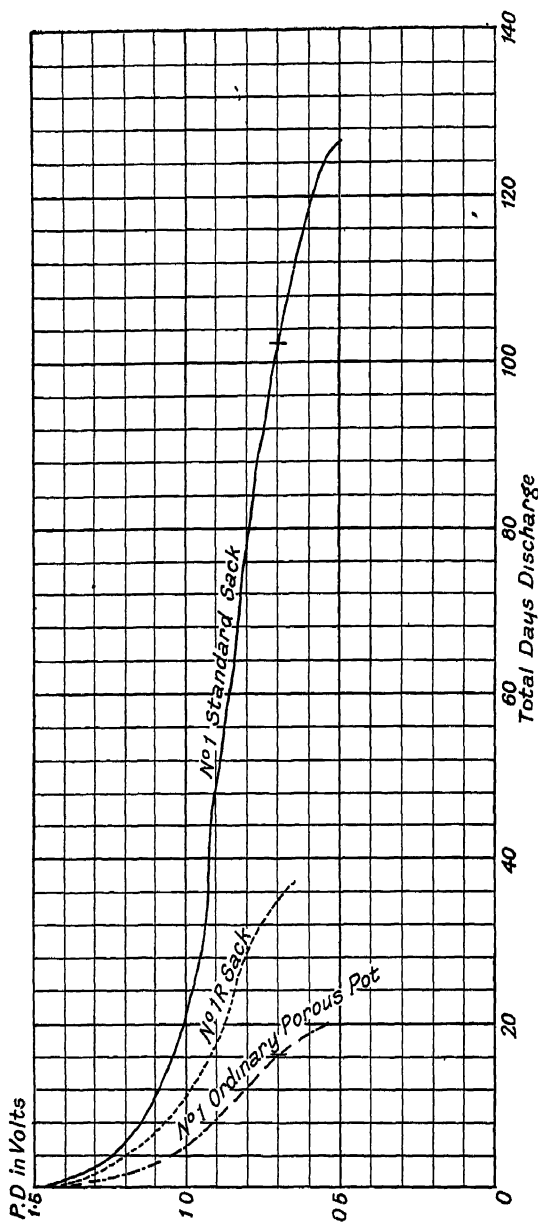


FIG 29 SIEMENS WET LECLANCHÉ CELLS THREE TYPES OF ELEMENTS FOR USE IN NO 1 SQUARE GLASS JARS ($4\frac{1}{2}$ IN SQUARE \times $7\frac{1}{4}$ IN. HIGH, EXTERNAL DIMENSIONS)

	External Dimensions	Average Output to 0.70 volt P D
No 1 Standard Sack Element	3 in dia \times 6 in high (body) or $7\frac{1}{4}$ in high (overall)	200 amp -hours
No 1 R. Sack Element	$2\frac{1}{2}$ in dia \times $6\frac{1}{2}$ in high (body) or $7\frac{1}{4}$ in high (overall)	75 amp -hours
No 1 Ordinary Porous Pot	3 in dia \times $6\frac{1}{4}$ in. high (body) or $7\frac{1}{4}$ in high (overall)	37 amp -hours

The test curves are from average figures taken during *continuous discharges* through 10 ohms external resistance, using a 15 per cent solution of ammonium chloride. The cells were kept free from excessive crystallization by cleaning the zinc electrodes and renewing the electrolyte as considered necessary

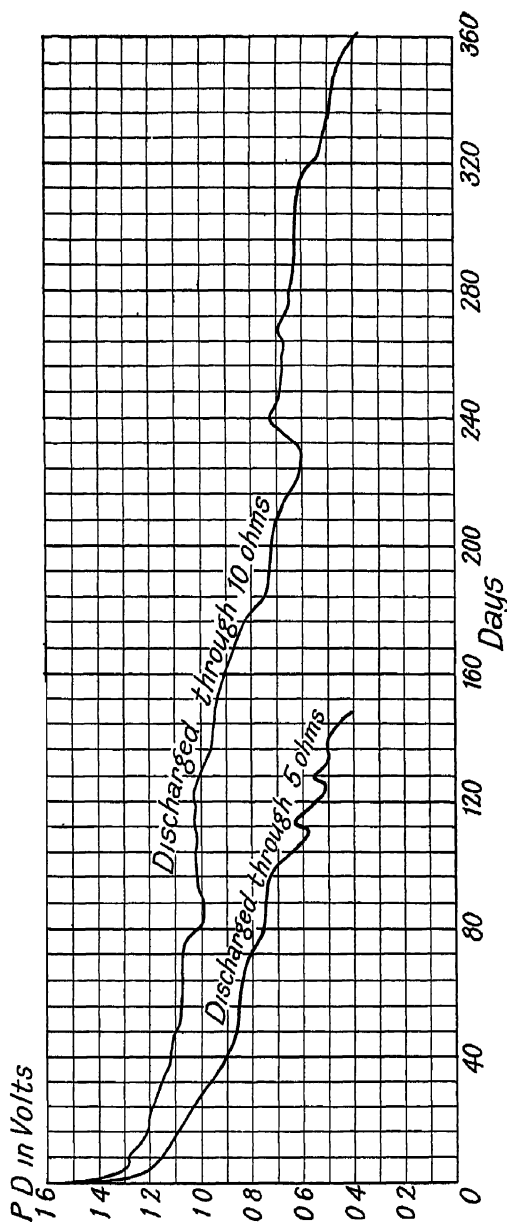


FIG 30 SIEMENS SACK CELLS SIZE No 00 AVERAGE TEST CURVES FOR CONTINUOUS DISCHARGES THROUGH 5 OHMS AND 10 OHMS RESPECTIVELY, USING A 15 PER CENT SOLUTION OF SAL-AMMONIAC AND CIRCULAR CUT-AWAY ZINCS

The solution was changed and zincs were cleaned as required during the course of the tests

Outputs in	5 Ohms Test			10 Ohms Test		
	To P D 1 volt	To P D 0.75 volt	To P D 0.50 volt	To P D 1 volt	To P D 0.75 volt	To P D 0.50 volt
Amp -hours	156	418	552	340	460	694
Watt-hours	173	388	447	370	479	597

author for a first-class No 2 sack cell similar to that illustrated in Figs. 24 and 25, from which it will be seen that the cell was not exhausted to 75 volts P.D until 770 hours, approximately, had elapsed Fig 27 (b) shows the curve of discharge for a similar cell, such is usually purchasable for bell ringing, the same electrolyte being used in each cell throughout, and not changed as advised by

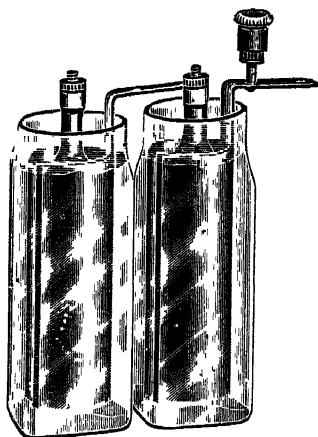


FIG 31A MINIATURE SACK CELLS
FOR RADIO ANODE CIRCUIT

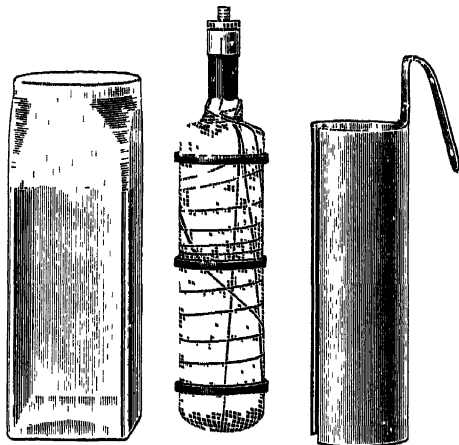


FIG 31B COMPONENT PARTS FOR
SMALL RADIO WET CELL

the makers from time to time Curves supplied by Messrs Siemens (Fig 28) show discharges from a No 2 porous pot element, and from a standard short sack and a 2R sack element, while Fig 29 gives similar interesting discharge curves for a No 1 porous pot element, and similar sizes of sack elements.

The discharge curves of the extra large size No 00 cell, illustrated in Fig 26, are shown in Fig 30, the discharges being through 5 and 10 ohms respectively It is interesting to compare the capacities in ampere-hours developed by similar cells at the higher and the lower rates of discharge

In contrast to such large sack cells, we may turn to

the not unimportant type of Leclanché illustrated in Fig. 31, that is, a miniature sack cell for the anode circuit of wireless sets made by the Wet H T Battery Co.

The illustration clearly depicts the small sack with its rubber insulating bands, and the cylindrical zinc which encircles it. The electrolyte recommended for this cell is sal-ammoniac, containing a certain amount of zinc chloride, which keeps the elements in good condition over the protracted intervals of rest which are naturally experienced with broadcast reception. To minimize evaporation, the makers advise the use of a little mineral oil floated on the surface of the electrolyte. These cells are made in various sizes to furnish up to 7, 14, and 30 ma. respectively, and are reckoned as exhausted at 8 volt.

The makers particularly emphasize the need for insulation between these cells, and the care which should be taken not to spill electrolyte over the outside of the containers when filling. Cells of this type are more satisfactory than dry batteries if portability is not of the first importance, and are easily set up and cheaply renewed when exhausted.

The Electrolyte.

A little care and attention in the preparation of the electrolyte for Leclanché cells will be repaid in future upkeep of the battery.

If the cells are to be used for heavy current outputs, a strength of about 6 oz. of sal-ammoniac to 1 pint of water (a nearly saturated solution) should be used.

A solution of this density will tend to form crystals when the cell is working strongly, and to creep up the sides of the jar, the sack, and the zinc when idling. This applies also to less dense solutions down to 4 oz. to the pint.

For normal working 3 oz. to the pint will be found quite efficient, while at the same time giving a minimum of creeping effect, this particularly applies to warm countries.

The strength laid down by the Post Office is a 15 per cent

solution, that is, 3 oz. of sal-ammoniac to 17 oz of water. In certain cases—where cells are totally enclosed—the Post Office favour the use of manganese chloride as an electrolyte in place of ammonium chloride, as this salt does not emit ammonia fumes tending to corrode brass fittings, etc.

Some manufacturers recommend special salts composed of a mixture of the chlorides of ammonium and zinc, the latter, being deliquescent, prevents creeping to some extent

The addition of sulphate of zinc to the manganese-carbon mixture has been tried by other makers with the idea of preventing the formation of crystals of zinc and ammonium oxychloride which is frequently troublesome in its growth. Further, as the zinc sulphate dissolves out, it renders the main depolarizer mass more porous

The growth of insoluble oxychloride crystals is caused by the weakening of the sal-ammoniac solution as it is turned into zinc chloride. The zinc chloride, being denser, falls to the bottom of the cell, and oxychloride crystals are deposited on the zinc and also on the porous pot or sack, as the case may be, and, being non-conducting, adds greatly to the I R. of the cell

Usually the solution of a high-grade Leclanché sack cell should be renewed two or even three times during its life to get the best results, avoiding thereby as much as possible the growth of the insoluble and non-conducting oxychloride formations which choke up the cell

The addition of a little mercury perchloride has been suggested to keep the zinc in good order and to discourage the growth of the oxychloride, but as this salt is extremely poisonous, its common use should not be entertained

When the zinc chloride above mentioned falls to the bottom of the cell it tends to set up a concentration cell about the zinc rod used (see p 17), with the consequence that such rods are nearly always attacked more strongly near the water-line, and tend to break off there before the rest of the rod is used up

To counter this, Messrs Siemens Bros and others use a cigar-shaped rod thickened at the water-line and furnished with a hook to hang over the edge of the jar (Fig 32)

Probably the best form of zinc is the short cylindrical pattern hanging from the jar, as this not only lowers the resistance of the cell, but, being suspended in the middle of the solution, avoids any loss which might be set up by the formation of a concentration cell in the electrolyte

Whatever form of zinc is used in Leclanché cells it should be of good quality, and rod zincs should be drawn—not cast—as cast zincs give inferior results. The British Post Office specifies that zincs supplied should contain at least $2\frac{1}{2}$ per cent mercury as amalgamation and be free from impurities. The diameter of a No 1 zinc rod is generally $\frac{1}{2}$ in, and that of a No 2 $\frac{7}{16}$ in, the former being provided with a terminal wire of 16 S W G copper, and the smaller with wire of 18 S W G.

For other details of Leclanché cells, see chapter entitled “Maintenance and Upkeep of Cells”

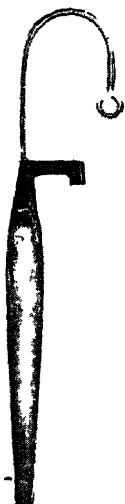


FIG 32
SIEMENS
NON-IN-
CRUSTING
ZINC

Lead Peroxide Cells.

Lead peroxide seems to have been first used practically by Reynier, who employed plates similar to those of an accumulator, and later by Harrison, who either compressed the peroxide round a serrated lead rod or held it in a basket-shaped grid. The solution is dilute sulphuric acid, and the anode well amalgamated zinc. Unlike most solid depolarizers, lead peroxide can give very heavy currents without any falling off in volume until the cell approaches exhaustion, also the E M F. is high (about 2.5 volt), but the cost of the peroxide is also relatively high, especially in view of the total ampere hours capacity obtained.

This type of cell has never been popular owing, probably, to the difficulty of leaving it on open circuit without excessive local action, the nature of the electrolyte (dilute sulphuric acid) acting on the zinc to some extent even when heavily amalgamated with plenty of free mercury

The use of bisulphate of soda in place of dilute sulphuric acid does not help much, and the substitution of any other of the usually known electrolytes considerably depreciates the action of the cell.

To counter the consumption of the zinc on open circuit, the author placed it in a solution of caustic soda within a porous pot, as a two-fluid cell

This arrangement gives a voltage of 3.14 volt, the cell being very active, but, unfortunately, the porous pot does not long survive

For experiments of this nature, well-charged accumulator plates act excellently, or the peroxide may be pressed round a lead or carbon rod within a porous pot, using either single-fluid or two-fluid electrolyte, but this arrangement is not so good as with the conventional lead grid, owing to poor contact and high internal resistance.

Several modifications of Reynier's cell have appeared from time to time, notably an ingenious cell of accumulator type in celluloid case into which a zinc bullet was dropped when it was required to "charge" the cell, but none appears to have survived

CHAPTER V

DRY CELLS

DRY cells are in reality Leclanché cells in which the electrolyte is immobilized so as to render them unspillable, the cell, of course, not being really "dry," but containing a modicum of moisture sufficient to allow the requisite chemical actions to continue their functions. Dryness is, indeed, one of the great enemies of dry cells, and much thought and experiment have been devoted to keeping the cell moist under all conditions of life and for considerable periods. When a "dry" cell becomes really dry it is useless, and there are few things more dead than a dead dry cell.

Usually, although not always, the zinc anode is in the form of a square or circular pot which also serves as the container, being usually surrounded by a layer of cardboard or papier mâché to avoid accidental short-circuiting when stood upon a metal surface. Occasionally the zinc is formed as a cylinder within a glass or earthenware container. The first successful dry cell was devised by Gassner in 1888, from which present-day cells are descended with detail improvements in manufacture.

This cell consisted of a zinc pot as above described, lined with a paste of plaster of Paris soaked in sal-ammoniac solution. Within this paste was placed centrally the carbon electrode, tightly packed with manganese dioxide and crushed carbon, also moistened with sal-ammoniac.



FIG 33 DANIA
DRY CELL
Atlas Carbon
and Battery Co

solution. The whole cell was then sealed with pitch, two small tubes being sealed in to allow the escape of any gases generated within.

Modern dry cells follow broadly two methods of manufacture, thus there are packed cells, mostly favoured in the

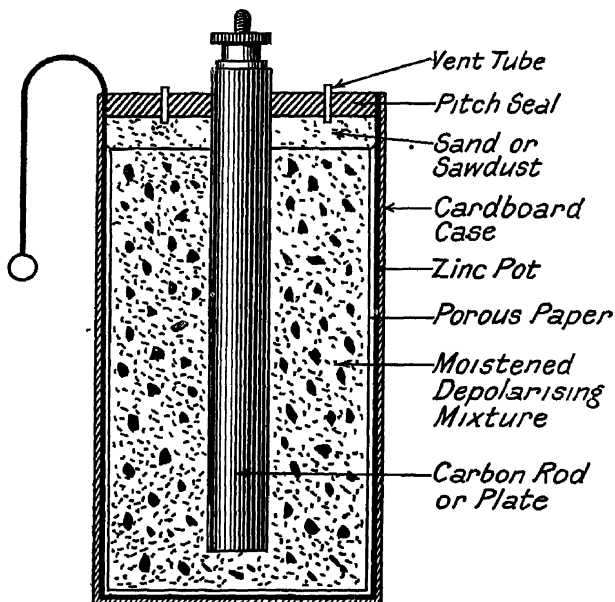


FIG. 34 DIAGRAM OF PACKED DRY CELL

U S A, and sack cells as usually made in Europe. Fig. 33 depicts such a well-known form of cell.

In the packed form of cell (Fig. 34) the zinc pot is lined with a few turns of moistened blotting paper or porous paper pulp, the carbon put centrally in place, and the annular space filled with the depolarizing mixture of manganese and carbon moistened with suitable electrolyte and rammed home tightly. The top of the cell then usually has a paper or cardboard washer fitted on, upon which is placed a layer of sand or sawdust, then another paper

washer, on which the usual pitch seal, with its two ventilating tubes, is poured

A cell of this kind has initially a very low internal resistance, and can give momentarily heavy currents of about 25 amp., but, apart from this somewhat useless

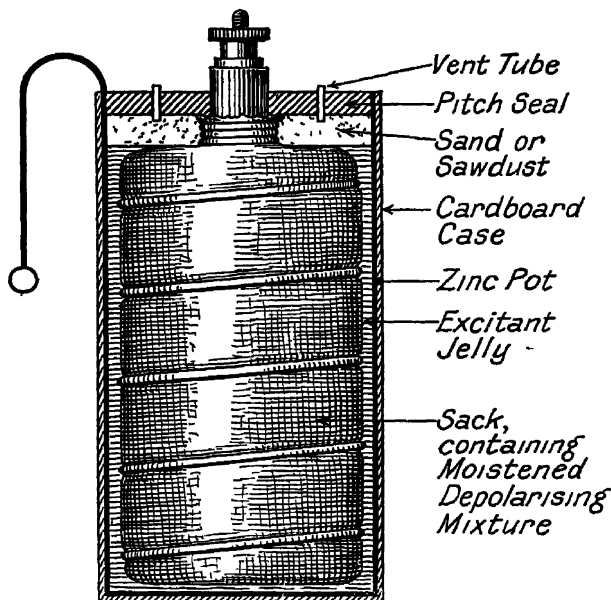


FIG 35 DIAGRAM OF SACK DRY CELL (DANIA TYPE)

feature, these cells are inferior to those constructed on the European plan, as they tend to dry up much more quickly than do properly constructed sack cells

In the sack type of dry cell (Fig 35) the manganese and carbon mixture moistened with sal-ammoniac solution is tightly compressed round the carbon electrode confined in a bag of woven material, such as mutton cloth. This element is frequently spoken of as the "dolly"

The depolarizing element is placed in the zinc pot, and the space between them filled in with either a white

plaster-of-Paris mixture or, more usually, a gelatinous compound

In the case of the manganese-carbon mixture this is usually a fairly fine powder, the carbon being either partly or wholly natural graphite, such as Ceylon graphite, to give good conductivity to the mass. The greatest care has to be exercised to make sure the bag wholly contains the depolarizing mixture, for should any of it escape and reach the zinc pot heavy local action would naturally ensue.

The white paste above mentioned usually consists of a mixture of roughly four-fifths plaster of Paris and one-fifth flour, or similar farinaceous substance, moistured with sal-ammoniac solution to which zinc chloride is frequently added as a deliquescent to keep the paste moist.

The paste may be allowed to set naturally in the pot, but in some cases it is also "cooked" by steam heat.

Most of the successful modern cells, however, use a gelatinous paste or jelly instead of the white plaster. This paste may have as its basis gum tragacanth, agar-agar, gelatine, dextrin, or other mucilaginous substance forming a slimy jelly. The excitant used is, as before, a solution of sal-ammoniac, to which are added frequently zinc chloride, glycerine, or calcium chloride, with the idea of keeping the jelly moist for long periods. Mercuric chloride is also sometimes incorporated in the mixture to help in amalgamating the zinc pot, and thus limiting local action and the growth of crystals.

The dolly of depolarizer is kept from touching the pot by strips of waxed cardboard or other suitable means, and sealed in with pitch. Usually an air space occupied by sand, sawdust, cork dust, etc., is arranged between the top of the active ingredients and the pitch, so that any gases generated when the cell is working may escape. This point is essential in a good cell because, although the gases must escape to avoid bursting the cell, the atmosphere must not have too free ingress or the cell may be unduly dried.

thereby For this reason dry cells should be kept at an equable temperature, otherwise extremes of heat and cooling will cause the cell to breathe through its vent tubes ; thus on exhaling there will be a loss of moisture, and on inhaling dry air will be drawn in to the detriment of the life of the cell. Dry cells when freshly manufactured have a comparatively low I R , but as they age, either by use or the passage of time, their internal resistance rises This is due either to the drying up of the excitant moisture, or to the formation of zinc hydroxide, or both If the formation of hydroxide is strong the cells frequently burst The addition of zinc chloride is supposed to neutralize the formations of the ammonium gas, and to retard the growth of hydroxide crystals.

Since a cell may not be called upon to give its output for some considerable time from the day of manufacture, a large amount of experience on the part of the maker is necessary in the choice of ingredients to ensure a reasonable output at the end of a long shelf life

Obviously, it is better to be satisfied with a cell of lower ampere-hour output if it will give that output at the end of, say, 18 months, rather than to choose a cell of higher output in ampere hours which may be uncertain in action at the end of 6 months This applies particularly to small dry cells used for wireless purposes, because they are frequently expected to give their output after relatively long periods of inaction, either due to being in stock at the dealers, lack of interest in the broadcast programme, holidays, or other causes, and the minuteness of the cells naturally does not help in the retention of moisture There is in such batteries arranged in sealed blocks the question of leakage between cell and cell Every precaution should be taken that there is adequate insulation, not only between each individual cell, but between each group of cells, and care must be exercised that such groups, when at considerable difference of potential, should not be adjacent.

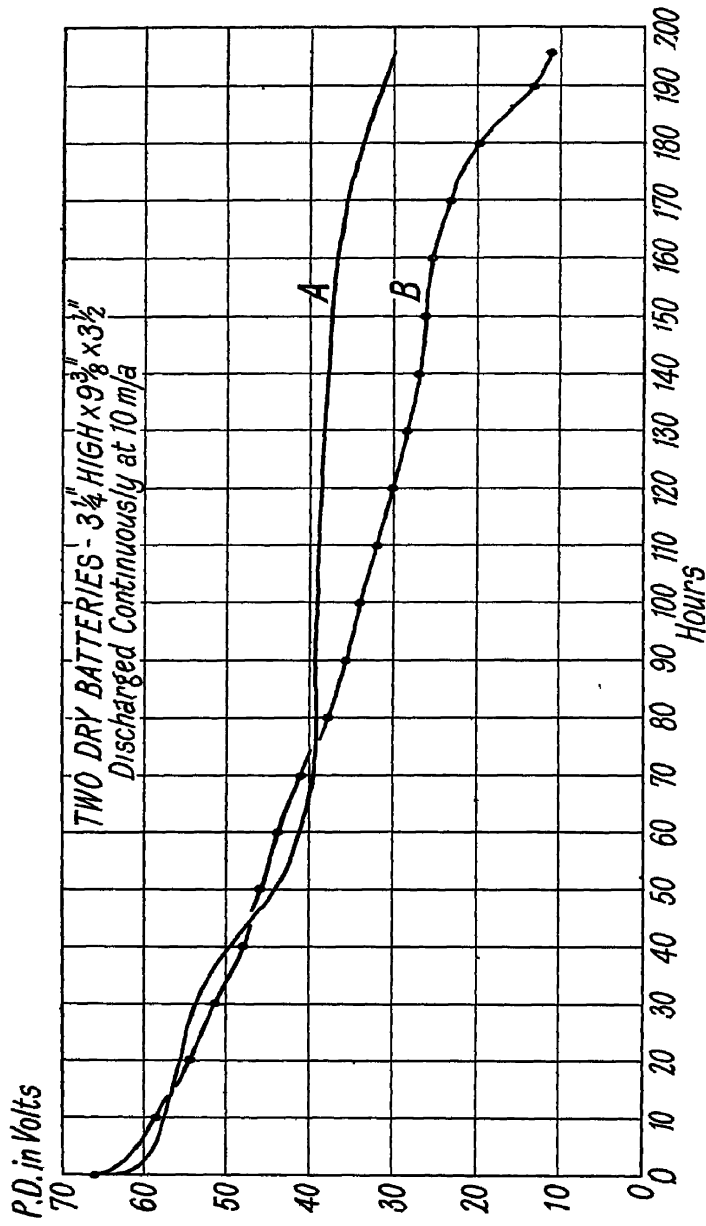


FIG 36. TWO DRY RADIO BATTERIES DISCHARGED CONTINUOUSLY AT 10 MA.

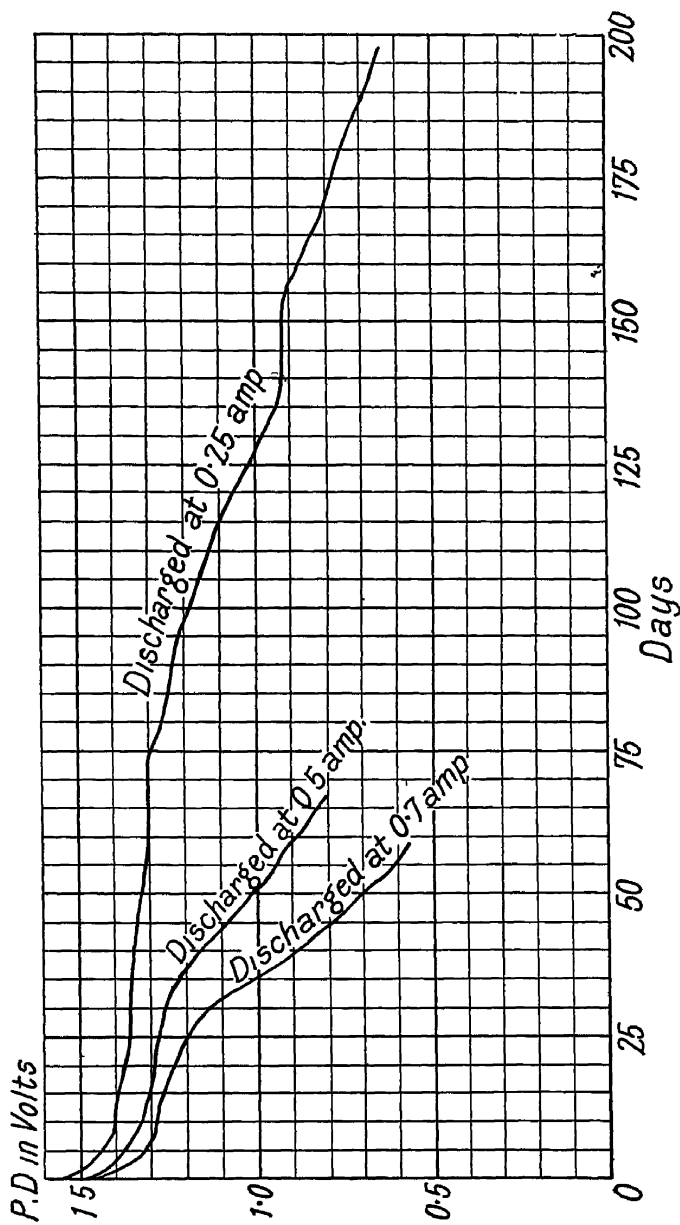


FIG 37 TEST CURVES ON A LARGE SIZE OF DRY CELL AS USED FOR L T FILAMENT CIRCUITS,
SHOWING THE EFFECT OF RATE OF DISCHARGE ON THE EFFECTIVE LIFE

In each case the cell was discharged for 3 hours continuously per day

Fig 36 gives the output curves of two well-known high-tension batteries of similar size

It will be seen that the battery which was at first the more powerful proves in the end less efficient than its competitor

This example shows how extremely difficult it is to judge the efficiency of a battery, either by taking its voltage or its short-circuit current.

A continuous discharge, to some extent, gives a comparative idea but destroys the battery under test, moreover, there is no guarantee that two batteries will behave even approximately in the same way, or that their behaviour will be alike at the end of 6 to 12 months. In this respect wet batteries score heavily over the dry variety, and are to be recommended when portability is not an essential point.

The rate of discharge of the batteries shown in the curve (10 ma) is rather severe, and it should be remembered that a better efficiency can be obtained from a dry cell by under-running than by over-running it, provided the current taken is not so low as to allow the whole time of discharge to play a preponderating part, that is, the cell should only be discharged at such a rate that it becomes as it were electrically empty before it becomes stale or dried up by time.

Fig 37 shows a curve of large dry cells suitable for filament heating discharged at various rates. It will be seen that such a cell lasts 155 days when discharged at $\frac{1}{4}$ amp for 3 hours a day, to .9 volt, but only 60 days at $\frac{1}{2}$ amp, and barely 40 days at .7 amp. Tabulated in ampere-days this is

		Ampere days of effective life
At	25 ampere	36
"	5 "	30
"	7 "	28

Hence, the economy of discharging a dry cell well within its limits is well demonstrated by these curves, in other

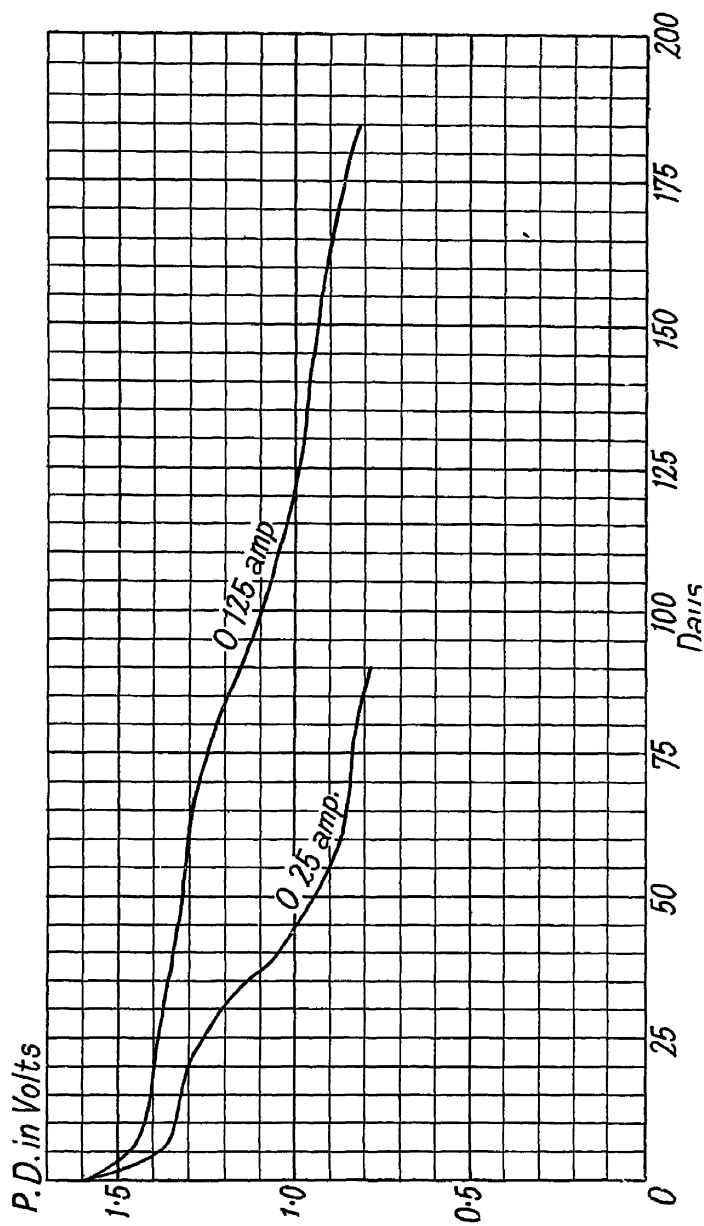


FIG 38 SIEMENS SPECIAL No 640 DRY CELL FOR WIRELESS L T FILAMENT CIRCUITS
Discharged for 3 hours per day at 0.125 amp, and 0.25 amp, respectively

words, for the higher rate of discharge a larger cell is necessary for true economy

Another concrete example is given in Fig 38, by curves supplied by Messrs Siemens Bros, of the discharge of one of their low-resistance circular cells, $2\frac{1}{2}$ in in diameter, and $6\frac{1}{2}$ in. high (Fig 39) Here the capacity falls from about 62 amp-hr when discharged at .125 amp., to 41 amp-hr approximately when the current is increased to 25 amp



FIG 39
SIEMENS
LOW RE-
SISTANCE
CELL
(CIRCULAR)

From these results the necessity of choosing a cell of ample size for the duty imposed can be realized, and this is particularly the case with such small cells as are used for flash-lamp purposes or for wireless high-tension batteries

It is not easy to obtain figures of discharge rates for these latter, because so much depends on circumstances, that is, on the total current taken by the set and on the periods of use and of repose. Taking these as being normal, Messrs Hellenes publish the tables given on the next page as a guide

Inert Cells.

Before terminating this chapter, mention must be made of an important branch of dry cells, that is, the inert cell, which is virtually a dry cell put up without the moist paste in place, and with one of the vent holes enlarged to form an opening large enough to carry a small cork (Fig 40) Although the paste is omitted as such, the excitant salts are left in place within the cell, and in some cases the desiccated components of the jelly Under these conditions the cell will store in good condition for very long periods, and when it is required to put the cell in action it is only necessary to add water through the vent (having removed the cork) till the cell is full, using for the purpose a small glass syringe similar to that used to fill a fountain pen

STANDARD CAPACITY

(MAXIMUM DISCHARGE ADVISED—8 MA)

Periods of Use	Rate of Discharge in Milliamperes			
	5	10	15	20
	Life in Hours			
30 hours per week	320	140	85	60
40 " "	300	130	80	55
50 " "	280	125	75	55
60 " "	250	115	70	50

DOUBLE CAPACITY

(MAXIMUM DISCHARGE ADVISED—12 MA)

Periods of Use	Rate of Discharge in Milliamperes			
	5	10	15	20
	Life in Hours			
30 hours per week	550	260	165	120
40 " "	540	255	160	115
50 " "	520	250	160	110
60 " "	500	250	155	100

TREBLE CAPACITY

(MAXIMUM DISCHARGE ADVISED—20 MA)

Periods of Use	Rate of Discharge in Milliamperes		
	10	15	20
	Life in Hours		
30 hours per week	430	280	200
40 " "	420	270	195
50 " "	410	260	185
60 " "	400	250	170

After the cell has stood for some time the excess of moisture, if any, can be shaken out, and the cell, re-corked, is ready for use. Cells of this sort should, in general, be used standing up, although for short periods they may be used in any position

The advantages of cells of this description for long storage or for tropical use are apparent, since deterioration

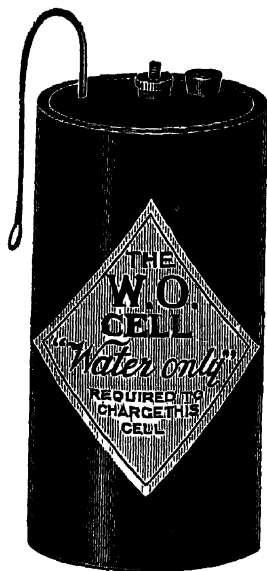


FIG 40. INERT CELL
Atlas Carbon &
Battery Co., Type
W O. (Water only)

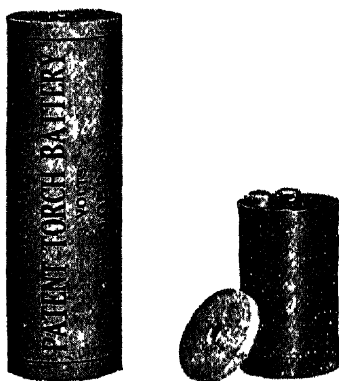


FIG 41 SIEMENS INERT
FLASH LAMP CELL

does not begin till the cell is actually in use, hence, the reliability of the cell is greatly increased

Messrs. Siemens Bros. have used this principle in the manufacture of small torch batteries (Fig 41). On receiving the cells it is only necessary to remove the cork and to fill with water as above outlined, allowing the cells to stand for 24 hours. In this case, however, the small cork is not

replaced, but a composition cork disc, or washer, having a central hole to fit the carbon, is forced in place within the edge of the zinc cylinder, thus sealing the cell. Paraffin wax may be melted over the cork as an additional safeguard if desired. Thus charged, one is in possession of a battery as fresh as if just manufactured.

CHAPTER VI

TWO-FLUID CELLS

WE now come to cells using two fluids with a porous pot to separate them, the one fluid being the depolarizer surrounding the carbon electrode, and the second fluid acting as excitant to the zinc

In all such cells the porous pot plays a most important part, and is also, unfortunately, invariably a point of weakness

As we have said, the function of the porous pot is mechanically to separate the depolarizer and the excitant, while at the same time it must permit interplay of the two chemicals and sufficient conduction of the electric current.

If the porous pot is of the open-pored type of good china clay, its resistance will be relatively low, but transference of the liquids will be marked, while a pot of a harder and less porous kind will more effectively separate the two fluids, but will have a higher resistance

A good white porous pot will show blotches of damp on the exterior in from half to $1\frac{1}{2}$ minutes from the time it is filled with water. The close-grained porous pots are much slower in responding to this test and are usually of a red colour

As the porous pot has to be a conductor as well as to separate the two constituent solutions of the cell mechanically, it is almost impossible to prevent a certain amount of transference of the one component fluid (generally the depolarizer) into the compartment which should be reserved for the excitant. Again, it is almost impossible to prevent the fall of the exciting fluid within the porous pot from passing by exosmosis into the depolarizer's compartment and so weakening it

The two actions should not be confused for, taking the Daniell cell as an example, we find that although the dilute acid round the zinc within the porous pot falls, yet there is a transference of copper which is deposited on the zinc in the opposite direction

A great amount of work has been done to attempt to

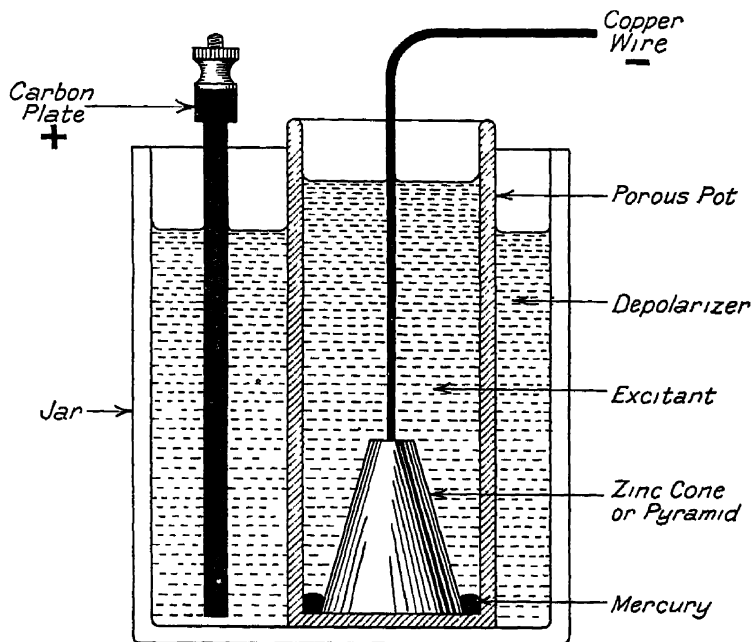


FIG 42 FULLER'S BICHROMATE CELL

check the diffusion of the liquids through the porous pot, whilst at the same time keeping it conducting

Impregnating the pot with collodion, gelatine, zinc oxide and chloride, soap, cuproammonium, etc, has been suggested, but with little success, the method invented by Darimont, to which we shall allude later, being probably the best to date

In addition to the disadvantages enumerated above the porous pot serves as an excellent path up which the salts used may climb by capillary attraction and crystallize out, thereby rendering the cell, sooner or later, useless. This disadvantage can be countered to some extent by dipping the edges of the porous pot for about 1 minute in

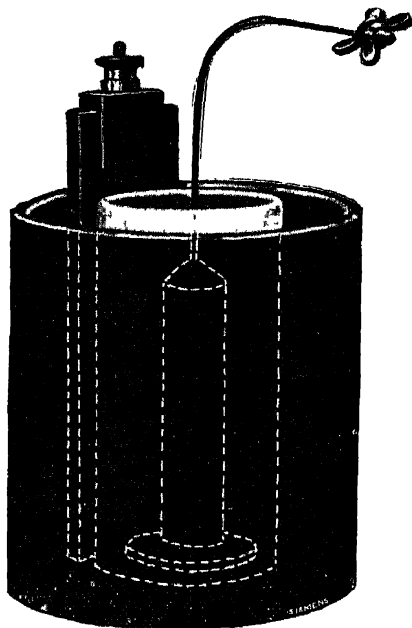


FIG. 42A FULLER TYPE 2-FLUID BICHROMATE CELL
(Siemens Bros & Co)

warm paraffin wax for $\frac{3}{4}$ in. in depth. There remains the weakness that porous pots tend to disintegrate in time, especially if alkaline solutions are used on the one side and acid or salt solutions on the other.

Two-Fluid Bichromate Cell.

Bunsen is reputed to have first suggested the use of potassium bichromate in a two-fluid cell, possibly as a

variation of the cell of his name, but the first practical model is due to Fuller (Fig 42) In this form the carbon electrode is placed in the outer container with the usual solution of potassium bichromate, sulphuric acid, and water Within the porous pot is placed the zinc, in this case a squat pyramid of zinc with a little free mercury to ensure good amalgamation The exciting solution may be dilute acid, zinc sulphate, or even plain water, according to the I R required of the cell In the case of plain water this becomes acidulated by a certain amount of transference from the outer or depolarizing solution The edges of the porous pot should be well waxed, and in Fuller's original cell about half of the cylindrical wall was also waxed to limit as much as possible transference between the two liquids Fig 42a shows the general appearance of such a cell, E M F about 2.01, as supplied by Messrs. Siemens Bros. The central zinc is in this case rather longer than in the original Fuller, giving a lower I R

It may be remarked here that sometimes the reversal of the elements is advocated, that is, that the carbon should be placed within the porous pot and the zinc without Since, however, the depolarizer is the more important of the two solutions a greater volume can generally be placed in the outer container than in the porous pot, and for this reason it is the better disposition of the electrodes and solutions

Using our Standard cell, 1 pint only of Ayrton's solution, as before, was placed in the outer container with two carbon plates 2 in wide

The porous pot was filled with about half a pint of dilute sulphuric acid (1 in 20), and a cylindrical zinc 5 in \times 4 in in area placed in the pot with a little mercury Fig 43 shows the curves of discharge at 1 amp and $\frac{1}{2}$ amp respectively The short-circuit current of this cell is now only 5 amp as against 13 of the single-fluid type, due to the I R. of the porous pot (I R. of cell about 45 ohm).

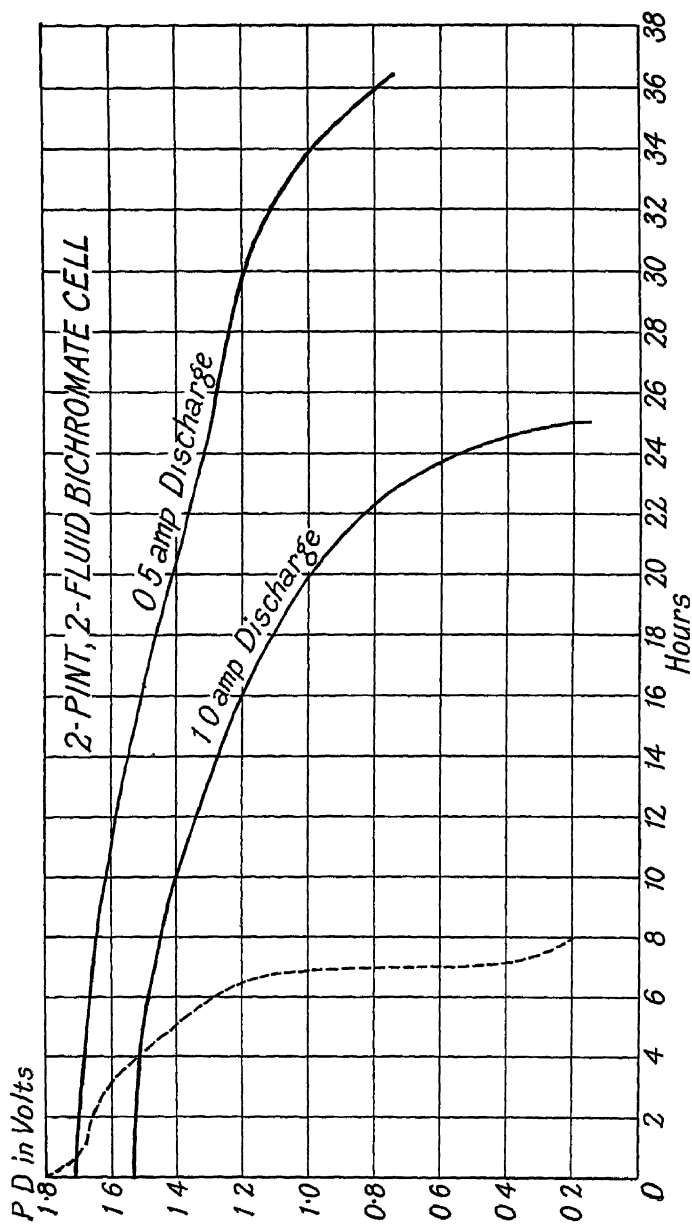


FIG 43 CURVES OF DISCHARGE AT HALF AND ONE AMPERE RATE OF 2-PINT 2-FLUID BICHROMATE CELL (DOTTED LINE SHOWS SINGLE-FLUID CURVE)

On the other hand the output of the cell in ampere hours is very much increased, and such a cell is extremely useful for general experimenting, or charging accumulators where a really strong current is required for several hours at a constant rate. The cell can also be left on open circuit for reasonable periods, and although, of course, it cannot compete with the sal-ammoniac type cell for open circuit work on feeble currents, yet Fuller cells will afford reasonable service for several weeks, also they are clean and cheap if properly looked after, and probably one of the best cells yet invented where moderately strong currents are required at irregular intervals. It should be noted here that all liquid depolarizers are far more rapid and energetic in their action than solid depolarizers in cells of comparable sizes. This is probably due to the fluidity of the depolarizer as a liquid in contrast to the fixed surface presented to the polarizing hydrogen by the solid depolarizer. Further, when the outer surface of a solid depolarizer is exhausted the hydrogen has to traverse the exhausted material before meeting fresh depolarizing surfaces, an objection which does not obtain in liquid depolarizers which are ever changing, due to convection and other causes. The acid exciting solution in the porous pot can be replaced by zinc sulphate or sodium bisulphate if desired, but, as already stated, the liquid in the porous pot will fall, and there will be a transference of the bichromate solution within the pot. In this case no very great harm will be done, especially if the zincs are wiped clean before using.

From the curves shown we see that at .5 amp discharge the ampere hours given were about 18, and at the 1 amp discharge about 22 to 8 volt. On the other hand, the P D of the smaller rate of discharge was maintained at an average of about 1.4 volts as against 1.24 volts with the 1 amp discharge, so that the watt-hours come out about the same, with a slight bias in favour of the smaller rate of discharge, as might be expected.

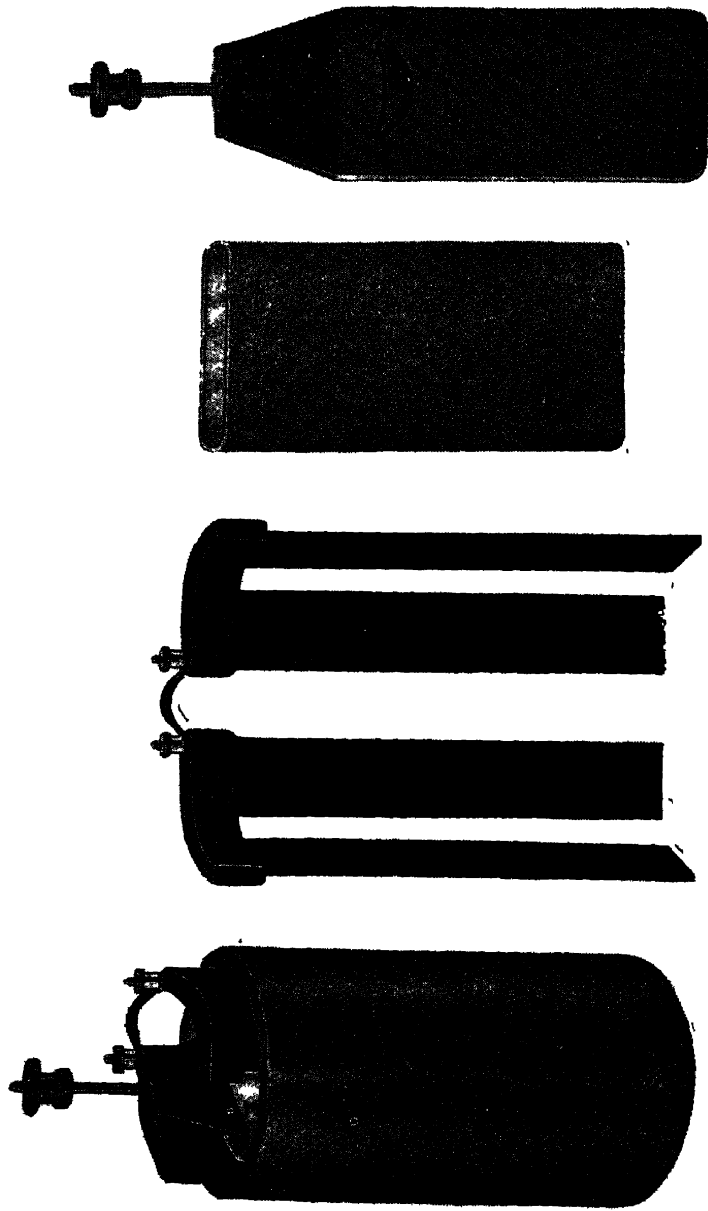


FIG 44 SILVERTOWN 2-FLUID BICHRIMATE CELL, SHOWING COMPONENTS

Both these performances easily surpass that of the single-fluid cell, whose curve is dotted in again for comparison, although only 1 pint of the same solution was used in the outer vessel against $1\frac{1}{2}$ pint for the single-fluid arrangement.

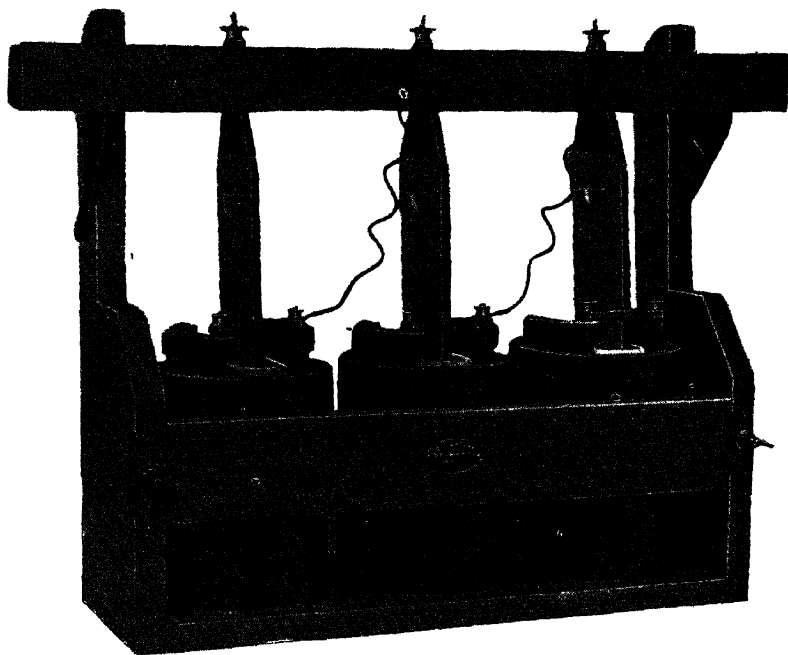


FIG 45 SILVERTOWN 2-FLUID BICHROMATE BATTERY, SHOWING
LIFT DEVICE

The superiority of the Fuller's type of cell is thus clearly demonstrated

Silvertown Cell.

Fig 44 shows a powerful form of bichromate cell supplied by the Silvertown Co. Owing to the large surface of the electrodes the internal resistance is very low. The pockets for mercury on the sides of the zinc should be noted.

Where several cells are used a frame is provided (Fig. 45),

whereby the zinc electrodes can easily be raised out of the exciting solution. Charges of crystals for these cells can be supplied ready mixed if required.

A 3-pint cell will give $1\frac{1}{2}$ amp for 20 hours continuously, and a 10-pint size 5 amp for the same period.

THE BLEECK LOVE CELL (E.M.F. 2.52 volts) is similar to the Fuller except that an alkaline electrolyte of caustic soda is used round the zinc as an excitant, the increased voltage being due to the Becquerel effect at the junction of the acid and alkaline solutions. The inventors add to the alkaline solution a little gum arabic to retard diffusion, and to the depolarizer, which is chromic acid and hydrochloric acid, a little ferrous sulphate. The idea may possibly be that the alkaline solution interacting with the ferrous sulphate in the pores of the pot will deposit a membrane of iron oxide, which will tend to stop diffusion and yet conduct.

This is undoubtedly the case, but diffusion is not sufficiently suppressed to qualify the cell for long open-circuit work.

The output in watt hours is fair, but except for its high voltage the cell is not as economical as the Fuller, and there is a tendency for a slime of chromium deposit to cover the zinc. In addition, the use of caustic soda is unpleasant, and the porous pots tend to disintegrate unduly, as is always the case when used with an alkaline and acid solution, as already explained.

THE BUNSEN CELL (E.M.F. about 1.95 volts) is probably the most powerful primary cell yet known.

The Bunsen cell is really a modified form of the cell first suggested by Grove, Bunsen substituting a carbon electrode in place of the expensive platinum plate first used by Grove. The cell consists essentially of an outer vessel containing the carbon electrode in a strong solution of nitric acid, and within the porous pot a zinc plate, usually in the form of a cylinder, with a solution of dilute sulphuric acid.

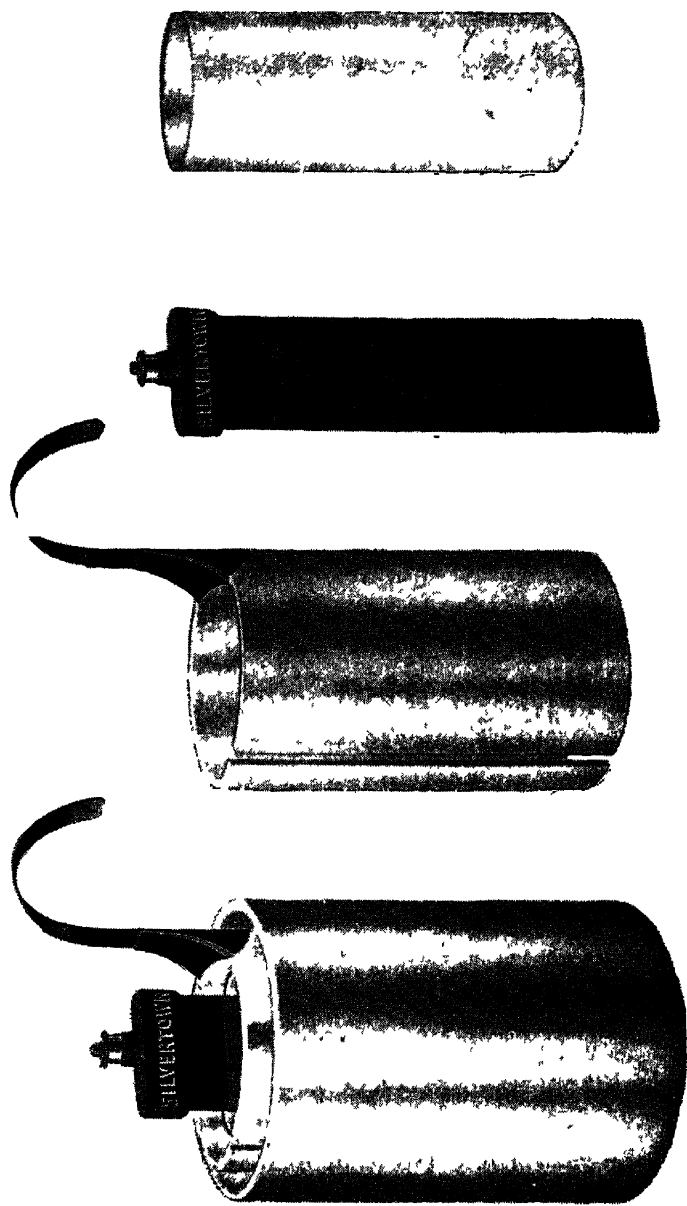
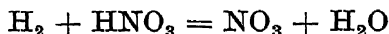


FIG 46. BUNSEN CELL WITH ITS COMPONENT PARTS

Fig 46 shows the general appearance of a Bunsen cell. In this case the carbon is centrally disposed within the porous pot, and the zinc is in the form of an encircling cylinder.

On the circuit being closed the sulphuric acid attacks the zinc, forming zinc sulphate and hydrogen— $\text{H}_2\text{SO}_4 + \text{Zn} = \text{ZnSO}_4 + \text{H}_2$

The hydrogen passing through the pores of the porous pot meets the nitric acid, and, combining with some of its oxygen, forms water and nitrous acid, thus,



By these means the hydrogen does not reach the carbon plate and polarization is prevented.

The chief objection to this cell is the offensive nitrous fumes given off by the depolarizer, which make it essential to use the cells in the open air only, and even then the fumes quickly corrode the terminals of the cells. Moreover, the virulent nature of nitric acid renders it an unpleasant material to handle.

With the Standard cell, the outer container was filled with 1 pint of strong nitric acid (S G 1.42), and two carbon electrodes 2 in. wide were used. The usual porous pot was immersed in the nitric acid, and contained a dilute solution (1 in 20) of sulphuric acid surrounding a cylinder made from sheet zinc, measuring 5 in. \times 4 in., and well amalgamated. The short-circuit current was 10 amp., and the I R of the cell about .25 ohm. Fig 47 gives the curve of discharge at 1 amp. It will be seen the current remains remarkably steady, and does not fall to 8 volt until over 40 hours have elapsed.

Various attempts have been made to improve on the Bunsen cell, thus a mixture of the nitrates of potash or soda and sulphuric acid has been suggested in place of the nitric acid, but these mixtures give comparatively weak results. D'Arsonval recommends the use of a depolarizing

mixture of nitric acid, hydrochloric acid, and water. Other suggestions were the substitution of bichromate of potash or perchloride of iron for the nitric acid, thus bringing us back again to the starting-point of other cells.

Callan and others constructed cells in which a cast-iron

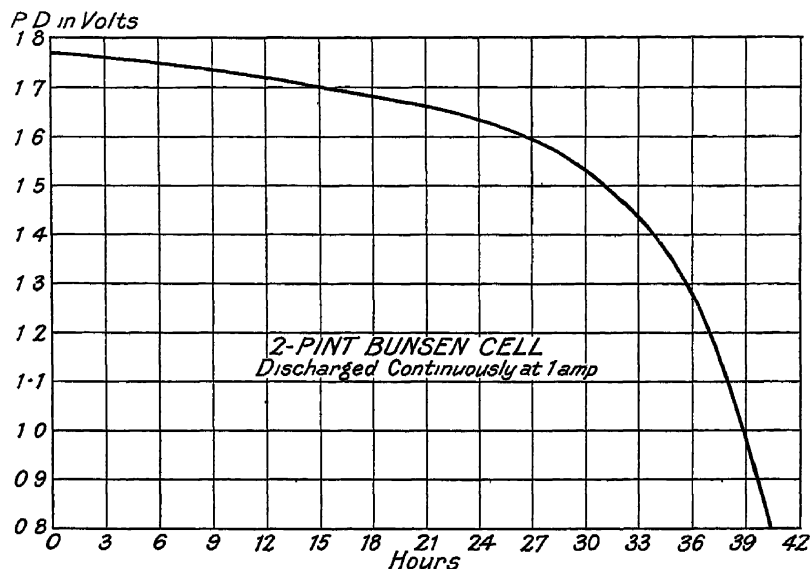


FIG 47 CURVE OF DISCHARGE OF 2-PINT BUNSEN CELL AT 1 AMPERE

container served at once the function of vessel and positive pole.

Cast iron, when immersed in strong nitric acid, assumes a passive state and is not attacked, but sometimes, notably if the solution weakens, the iron is acted on and the cell is likely to boil over.

DANIELL CELL This cell, originally suggested by Becquerel, was first evolved in its practical form by Professor Daniell.

It consists (Fig 48) of an outer vessel containing a copper

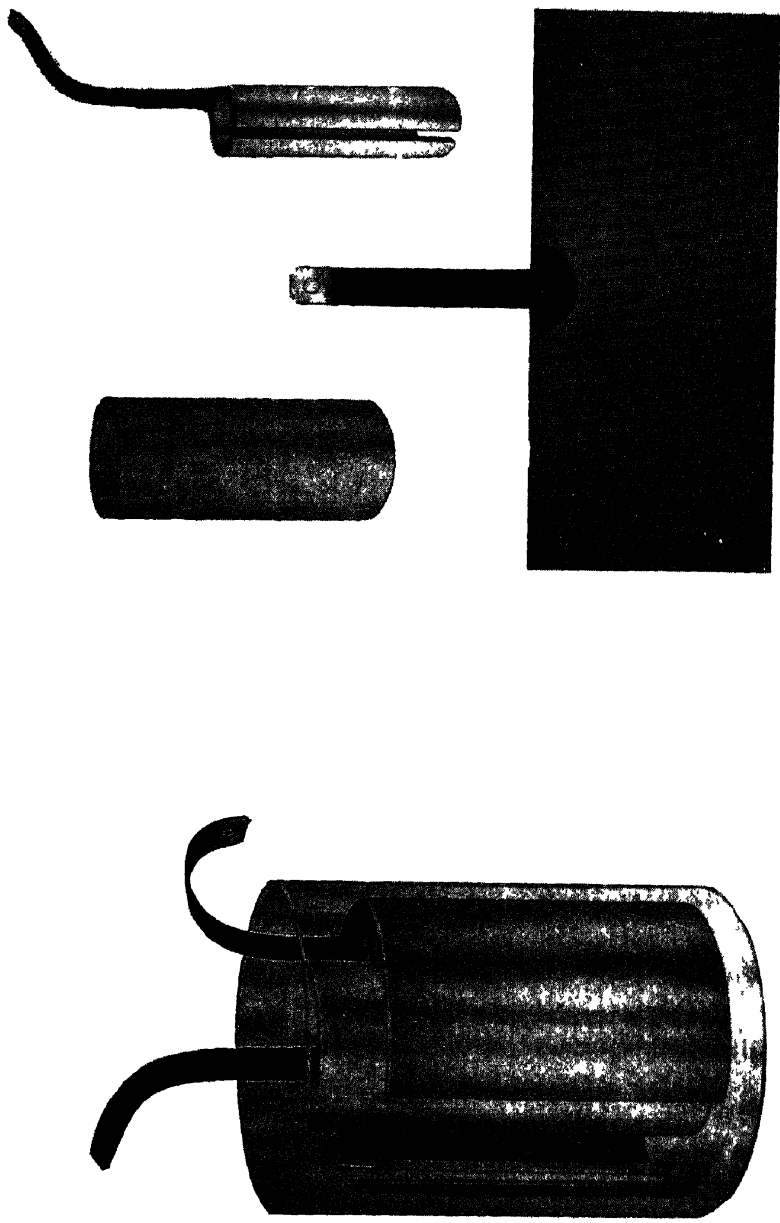
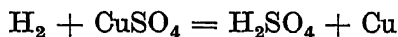


FIG 48 DANIELL CELL WITH COMPONENT PARTS
The Silvertown Co

plate in a concentrated solution of copper sulphate or bluestone. Sometimes the container is itself made of sheet copper, so as to act both as container and electrode. The copper plate is usually in the form of a cylinder, and within this is placed the porous pot containing a dilute solution of sulphuric acid and a zinc plate, rod, or cylinder

The action of the cell is as follows as before, the dilute acid attacks the zinc, forming zinc sulphate and generating hydrogen gas which passes through the porous pot to encounter the solution of copper sulphate when the hydrogen atoms are exchanged for those of copper Thus,



The result is that the copper sulphate solution is weakened to sulphuric acid, and metallic copper is deposited on the cathode or copper plate

This action continues until the whole of the copper sulphate is used up, the cell remaining extremely constant. In practice, it is usual to add lumps of copper sulphate to the solution to enable it to remain saturated, and, where great constancy and small local action are required, zinc sulphate should be added on starting the cell instead of dilute acid solution

The E M F of the Daniell cell is about 1.07 volts with strong zinc sulphate, and 1.1 volts with dilute sulphuric acid

Instead of zinc sulphate, magnesium sulphate, sodium bitartrate, salt, sodium bisulphate, and magnesium sulphate have been used. In the so-called Leclanché-Daniell sal-ammoniac is substituted, but there is little difference apparent in the action of the cell. With zinc sulphate it is hardly necessary to amalgamate the zinc as with dilute acid and other of the more violent excitants

With our Standard cell the outer container was filled with a concentrated solution of copper sulphate, made by bringing up about 6 oz of copper sulphate to 1 pint with water

In the outer compartment was stood a cylinder of sheet copper, $4\frac{1}{2}$ in \times 9 in, surrounding the porous pot which contained a $\frac{3}{8}$ in. zinc rod in the usual dilute solution of sulphuric acid (1 in 20). Such a cell, when new, gives about 1 amp on short circuit, and has an I R of about 46 ohm, which rises as the cell becomes exhausted to about 18 ohms.

Fig 49 shows the curve of discharge, from which it will be seen the P D remains remarkably constant during the whole run.

The cell can be recharged almost to its first freshness by adding more crystals of copper sulphate.

Apart from evaporation, the Daniell cell has three main faults. Firstly, copper is liable to be deposited on and in the porous pot whenever the copper or the zinc touches it.

The copper sheet, or the spiral of copper wire which forms a cheap substitute, should be arranged clear of the porous pot. This means an increase in internal resistance, but this is relatively unimportant, moreover, it allows a free circulation of the copper sulphate solution. The porous pot should be well impregnated with wax at the bottom as well as round the mouth of the pot, so that copper will then not be deposited at the two places where the zinc usually rests.

The second defect is the falling of the zinc sulphate excitant in the porous pot, and the consequent dilution and rising of the copper sulphate solution which may even rise enough to flood back into the porous pot.

Thirdly, there is the transference of the sulphate of copper into the porous pot, and its consequent deposition on the zinc, causing heavy local action. It is therefore necessary occasionally to clean the zincs, to replenish the excitant in the porous pot, and to withdraw by means of a syringe or syphon the copper sulphate solution if it rises too high, adding fresh crystals when necessary.

Innumerable modifications of the Daniell cell have been made, but without any great improvement. One of the

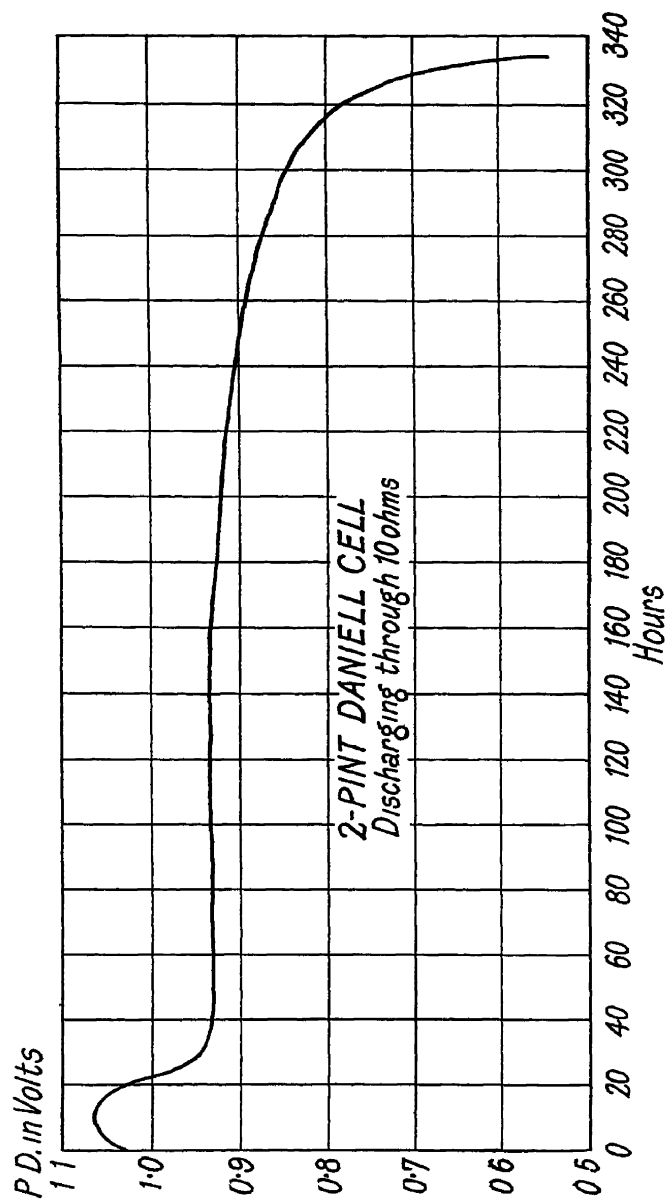


FIG 49 DISCHARGE CURVE OF 2-PINT POROUS POT DANIELL CELL ON 10 OHMS

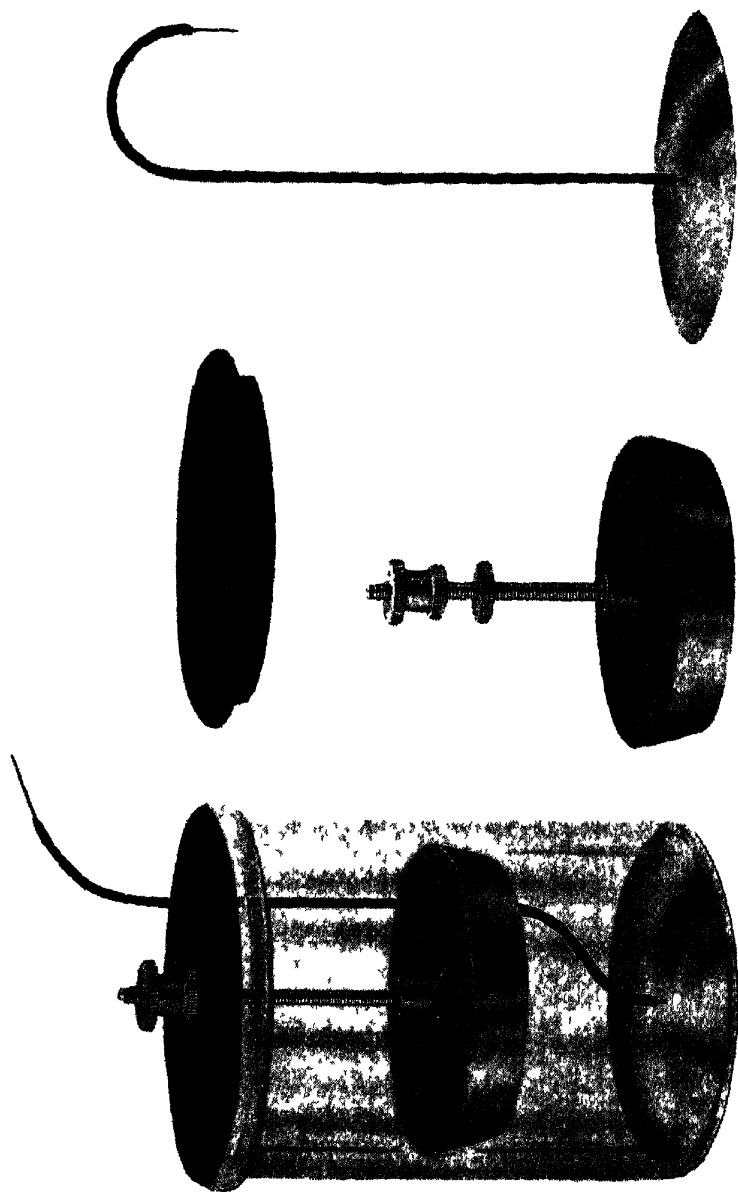


FIG 50 GRAVITY DANIELL CELL WITH ITS COMPONENT PARTS
(The Silvertown Co.)

most practical forms is known as the Gravity Daniell (Fig 50).

It will be seen this consists of a vessel, at the bottom of which is placed a copper plate, or spiral, leading to the surface by means of a rubber insulated wire. At the mouth

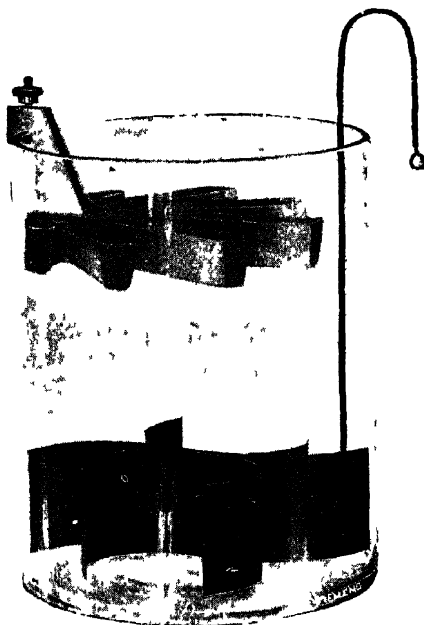


FIG 51 GRAVITY DANIELL CELL, CROWFOOT FORM
(Messrs Siemens Bros & Co)

of the vessel hangs the zinc electrode in the shape of a wheel or other similar configuration, according to the fancy of the maker. Copper sulphate crystals are placed at the bottom of the cell on the copper plate, and the vessel gently filled with a solution of zinc sulphate to the level of the zinc.

As the copper sulphate enters into solution its greater density causes it to lie at the bottom of the cell covering

the copper plate, and thus leaves a clear zone of zinc sulphate surrounding the zinc. By this means the porous pot with its attendant resistance is eliminated, as is the deposition of copper in the porous pot itself. Nevertheless, there is a certain amount of transference still with this arrangement, even if the cell is kept (as it should be) on closed circuit, and it is necessary occasionally to clean the zinc as well as to add crystals from time to time.

The zinc sulphate also should be partly withdrawn if it becomes too dense. Fig 51 shows another arrangement of gravity cell, known as the Crowfoot pattern, it is similar to the foregoing wheel type but has no lid. Many forms of gravity cell have been designed, notably by Kelvin, Callaud, Meidinger, Lockwood, Gethins, and others.

The Meidinger, or balloon type of gravity Daniell cell, is illustrated in the Frontispiece. It will be seen the copper cylinder is placed at the bottom of the cell surrounding the neck of an inverted bottle or balloon containing copper sulphate crystals and water. On a ledge or gallery towards the top of the cell is placed a zinc cylinder. The cell is filled with a solution of magnesium sulphate (about 1 part of salts to 5 or 6 of water by weight). As the copper sulphate solution at the bottom is used up, fresh crystals of copper sulphate fall down from the balloon and keep up the strength of the solution below, on the principle of a chicken feed fountain.

Gravity cells are naturally not very portable, and on that account we shall mention one remaining arrangement of Daniell cell intermediate between the gravity and the porous-pot form, viz, the Minotto (Fig 52). This cell is similar to the gravity form in that it has a copper plate at the bottom covered with copper sulphate, but on this is placed a layer of felt or canvas, and upon this is poured sand or sawdust to a depth of about 2 in. On this, again, is placed a second disc of canvas, upon which rests a flat plate of zinc with a suitably raised terminal. Zinc sulphate

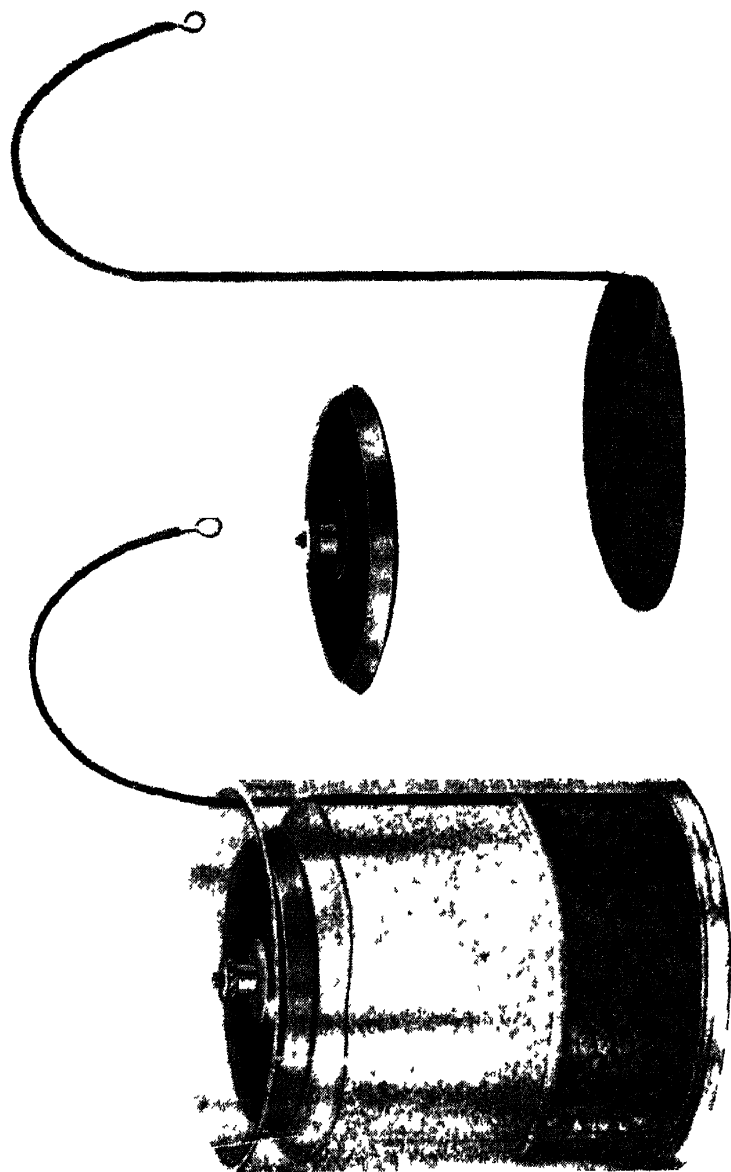


FIG 52 MINOTTO DANIELL CELL WITH COMPONENT PARTS
(The Silvertown Co.)

is poured in until the sawdust is saturated and the copper sulphate crystals sufficiently moistened for the cell to start work.

Such a cell has a very high internal resistance, some 10 or 20 ohms, but for telegraph and similar work this is of no great consequence

REYNIER CELL Reynier modified the Daniell cell by using caustic soda instead of zinc sulphate as the excitant. The E M F. is thus raised (owing to the Becquerel effect) to 1.65 volts. This cell also is relatively more powerful than the Daniell, and does not usually suffer from the bugbear of copper depositions on the porous pot. It is to be recommended for moderately strong currents over, say, a month's duration, but after that time the porous pot will tend to crack, diffusion and transference become marked, and the cell useless. The author has used copper nitrate successfully in place of copper sulphate with a slight rise in E M F (1.72 volts). Copper nitrate is also very much more soluble than the sulphate, but it is also more expensive.

FERRIC CHLORIDE CELLS Buff, Duchemin, and Marron appear to have used two-fluid cells, in which the carbon was immersed in a solution of ferric chloride (iron perchloride) and zinc in the porous pot with a solution of salt (sodium chloride) or dilute acid. Such a cell gives an E M F of 1.5 volts, and is very constant and powerful. The disadvantages of such a combination are that, owing to transference, iron is deposited on the zinc, and exosmosis tends to empty the porous pot and dilute the depolarizer, so that the cell is not of much use for any run extending longer than a fortnight. The author has found a solution of magnesium chloride gives superior results to salt or zinc chloride where strength of current is the first consideration, on the other hand, zinc chloride diminishes exosmosis and transference to some extent at the cost of a slight fall in E.M.F. D'Arsonval modified the cell by using caustic soda in place of the salt solution round the zinc, thus raising the

voltage of 2.12 volts, but the same difficulties arise and, in addition, the porous pot tends to disintegrate

Darimont appears to have been the first to have discovered a definite and satisfactory solution of the problem. In his cell (Fig 53) he uses the same solution as Duchemin and Buff, but adds to the salt excitant some anti-acid

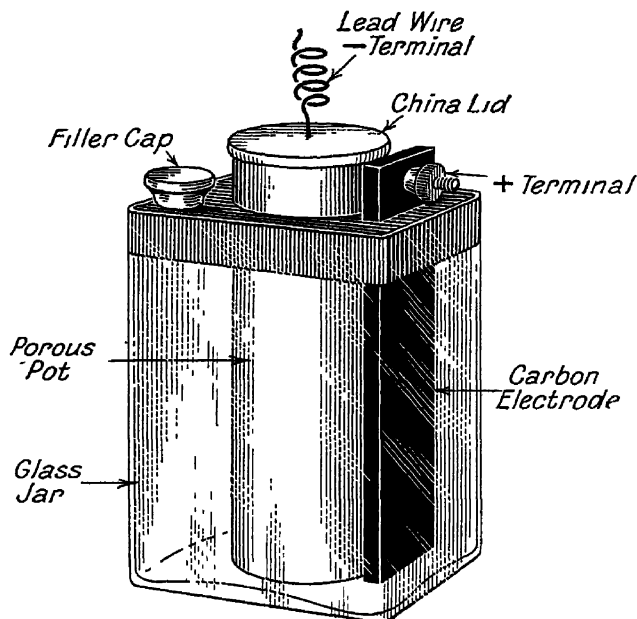


FIG 53 DARIMONT 2-FLUID FERRIC CHLORIDE CELL

material, such as chalk. As the perchloride of iron penetrates the wall of the porous pot, combination with the chalk takes place, forming an insoluble material which acts as a conducting, but semi-pervious, membrane. To keep the chalk in a state of suspension and prevent it falling to the bottom of the pot, the salt solution is also mixed with a mucilaginous agglutinant, such as starch or cornflour. To prevent the membrane being too deeply

formed in the wall of the porous pot, thereby unduly increasing the I R of the cell, chromic and/or hydrochloric acid can be added to the ferric chloride. The E.M.F. of this cell is 1.6 volts, and a steady and well-maintained curve of discharge, characteristic of ferric chloride cells, is given.

It is claimed that the membrane formed under the conditions just explained both prevents exosmosis from the porous pot and transference of iron to the zinc electrode, consequently, these cells can be left if desired on open circuit for really extended periods without deterioration.

CHAPTER VII

MAINTENANCE OF BATTERIES

THE care of batteries, particularly where there is a large number of cells, is essential to economical working.

Generally speaking, batteries should be installed in conditions where they can be left at a cool equable temperature, and where they are easily cleaned and ventilated

Extreme changes in temperature lead to excessive variations in the internal resistance of the cells, a complaint to which some cells are particularly susceptible. Cleanliness and ventilation are also necessary to avoid leakage through creeping, and discontinuities due to dirty or corroded terminals

Care of Leclanché Cells.

The greatest enemy of Leclanché cells is evaporation and consequent creeping of the salts up the sides of the glass jar and up the walls of the porous pot or the sack. Cells should be periodically inspected, and fresh water added as may be required. With air depolarizing cells the carbon electrode should be moved now and again to break away any crystalline formations which may form gas pockets

Creeping of salts up the jar and pot can be countered to a large extent by dipping the neck of the jar and the top of the porous pot in warm paraffin wax. The evolution of ammonia gas from the cell is liable to attack the brass terminals of the carbon electrode and the copper wires from the zincs, especially if the cells are in a confined space. It will be found helpful to brush the terminals with a little vaseline, or a half-and-half mixture of turpentine and castor oil.

When setting up Leclanché cells it is advantageous to allow them to soak for 24 hours in their sal-ammoniac solution before putting into use.

With porous pot cells, the absorption of the solution can be expedited by drilling one or two holes through the bottom of the pot with a small twist drill to allow the solution to enter more readily

As the cells age it will be found necessary to change the electrolyte and refill with fresh solution of the correct density (see p 65) This should always be done immediately there are any signs of the formation of crystalline or tree-like growths of oxychloride salts ; at the same time the zincs should be inspected and, if necessary, renewed It will be found sufficient to remove any white growths of oxychloride if the pots or sacks are scraped with a piece of blunt wood and the zincs with a knife In the event of the cell working irregularly a bad contact between the carbon and its cap should be suspected, owing to the formation of lead salts if the cap is of lead, or verdigris if the screw terminal is moulded into the carbon (see Carbons, later)

When the cell is exhausted most of the components, except the jar, must be thrown away The zinc, if in good condition may be cleaned and used again, but the porous pot or sack is practically valueless, as the carbon electrode cannot be used again in a first-class cell owing to the zinc oxychloride deposit within its pores Such carbons can only be utilized by grinding down and remoulding

The glass jars can be cleaned from hard chalk-like deposits by soaking them in a dilute solution of hydrochloric acid.

Dry cells do not call for much attention, beyond keeping them in a cool place at an equable temperature

When they are exhausted the more economical of our railway companies follow the plan of stripping off the cardboard covering, piercing holes in the zinc pot with a

bradawl, and setting them up as a wet cell in sal-ammoniac solution in a glass container. The solution percolates into the cell and gives a further lease of life. When the zinc pot is entirely used up the cells are sometimes again recovered by taking off the remains of the zinc pot and the surrounding jelly, and setting up the cell as a plain sack cell with fresh solution and a new cylinder or rod zinc. Of course, at this stage the cells are somewhat exhausted, but sufficiently strong to furnish currents for telephone use, etc.

CARBONS are made in two varieties, the older being of the cut variety, that is, the carbon rods or plates are cut from retort coke by means of a rotating disc loaded with wet grit. These carbons are the best where strong acids are used, such as in the Bunsen cell, but are naturally expensive.

The second kind, which are now almost universally used in ordinary cells, consist of carbon plates moulded from powdered carbon made into a stiff dough with syrup or tar and then baked in a furnace. In some cases the terminal screw is inserted in the dough before baking. Messrs Siemens insert the screw in a prepared hole and run it in with special alloy. The commonest method is to cast a lead cap over the end, either drilling holes or forming notches in the plate or rod so as to keep the cap into place. Still another way is to mould the head of the carbon with a bridge through which the shank of the terminal screw is inserted, a flat nut being tightened up under the bridge. This method allows the terminal to be removed for cleaning and inspection.

For experimental work it is sometimes convenient to copper-plate the end of the carbon, which can easily be done, and then to solder on the requisite metallic terminal or connector.

The carbon having been capped by any of these methods should be placed head down into hot paraffin wax for a few moments, so as to prevent creeping of the electrolyte

Should the electrolytic salts of whatever nature reach the junction of the carbon and its metallic connection, increased resistance growing to discontinuity must infallibly be expected, because non-conducting metallic salts will be formed.

As above remarked, Leclanché carbons should not be used a second time for Leclanché cells, but they may be used, after cleaning with sandpaper, quite satisfactorily in bichromate, ferric chloride or similar cells if desired, owing to the superior conducting and depolarizing powers of such cells

ZINCS have been freely illustrated throughout this book, but a word may be said about the quality

It is usually held that for Leclanché type cells the zinc rod should be drawn or pressed, and the Post Office specifies not more than 1 per cent of total impurities. Although this degree of purity may be desirable for Leclanché cells, it is by no means necessary for other primary cells in which ordinary commercial zinc sheet or cast spelter can be used, provided it is suitably amalgamated in the ways already indicated

Zinc can be easily melted in a small crucible or ladle over a gas ring, and cast either in a chill or a mould made of *well-dried* plaster of Paris or fireclay. By using the Fuller form of pyramid scraps of zinc and condemned zinc rods, etc., can economically be used again, a little mercury being *cautiously* added to the molten zinc, which should not be too hot or the mercury will be partly driven off as vapour.

CONTAINERS are usually of the glass variety, but sometimes glazed earthenware is used

Earthenware should be looked on with suspicion, as the electrolyte has a way of percolating through even the best glaze if there is a slight crack or crazing. This is particularly noticeable with ferric chloride and caustic soda. Ebonite and celluloid form good light substitutes for experimental cells.

Care of Two-fluid Cells.

The efficient working of bichromate and similar cells depends on keeping the components, particularly the porous pots and carbons, clean and in good condition

To this end it is wise to have handy a large earthenware trough or glass accumulator box, containing dilute hydrochloric acid, into which the porous pots and carbons can be placed to wash them clean. Porous pots from Daniell cells may need the addition of nitric acid (forming with the hydrochloric acid *aqua regia*) to free them from any deposited metallic copper

After, the pots and carbons should be stood in plain water overnight to rinse. If nitric acid is used to wash carbons beware of a momentary fictitious voltage when the cell is first set up again, as the nitric acid remaining in the pores of the carbon may give a higher voltage than the form of cell warrants. When mixing bichromate or other solution into which sulphuric acid enters, remember always to pour the acid slowly into the bulk of the solution and not vice versa

A very useful accessory for batteries is a syringe made from a glass tube, drawn to a nozzle at one end and furnished at the other with a large rubber bulb. With this adjunct liquid can be taken out of cells from the top without disturbing the contents, or with gravity cells strong copper sulphate solution, etc., can be added without disturbing the superimposed level of zinc sulphate

Finally, have handy a 2-pint measure glass and a reasonably accurate weighing balance. Never guess when making up solutions, even for the most obscure Leclanché cell.

USEFUL DATA

1 Pint of Water	{	= 20 fluid ounces
		= 20 ounces avoirdupois
		= 34.68 cubic inches
		= 568.24 cubic centimetres

ELECTRO-CHEMICAL EQUIVALENTS

<i>Element</i>	<i>Grammes deposited per ampere-second</i>
Hydrogen000010384
Aluminium0000932
Magnesium	0001242
Iron (ferrous)	0002902
Iron (ferric)	0001935
Copper (cupric)	0003281
Copper (cuprous)	0006562
Zinc	00033698
Mercury (mercuric)	0010374
Mercury (mercurous)	0020748
Silver	0011181
Tin (stannic)	0003058
Tin (stannous)	0006116
Lead	0010716
Nickel	0003043

TABLE OF SOLUBILITY IN 100 PARTS

(of common battery salts)

(The values given below are approximate and depend upon temperature)

Alum (potassium)	5.63
„ (sodium)	103.1
Ammonium carbonate	100
„ chloride	29.4
Calcium chloride	117.4
Chromic acid (trioxide)	163.4
Copper nitrate	243.7
„ sulphate	32.96
Ferric chloride	246
„ nitrate	V soluble

TABLE OF SOLUBILITY IN 100 PARTS—(contd.)

Ferric sulphate	V. soluble
Ferrous chloride	160.1
„ nitrate	200
„ sulphate	32.8
Magnesium chloride	187
„ sulphate	76.9
Manganese chloride	151
Mercuric chloride	6.5
„ nitrate	V. soluble
Mercurous nitrate	V. soluble
Potassium bichromate	4.65
„ bisulphate	36.3
„ carbonate	169.2
„ chlorate	3.3
„ chloride	34
„ hydroxide	13.3
„ nitrate	13.3
„ permanganate	2.83
„ sulphate	11.1
Sodium bichromate	239
„ bisulphate	28.6
„ carbonate	21.33
„ bicarbonate	9.6
„ chloride	35.7
„ hydroxide	109
„ hyposulphite	18.1
„ nitrate	87.7
„ sulphate	36.82
Tartaric acid	115
Zinc chloride	209
„ nitrate	324.5
„ sulphate	143.3

The figures on page 112 are taken from Professor Ayrton's *Practical Electricity*, and give the theoretical weight of material consumed in various cells. With perhaps the exception of the zinc, these figures are very different in practice, owing to the losses in the cell, and also to the fact that in the tables the current is apparently calculated to zero voltage, while in practice the cell is usually discarded at half its original potential. The figures form, however, an interesting basis of comparison between different cells, and a useful guide when mixing solutions.

APPROXIMATE WEIGHT OF MATERIALS CONSUMED
PER 1000 AMPERE-HOURS

		lbs
Daniell	Zinc	2 69
	Copper sulphate (copper produced)	10 3 (2·61)
Grove or Bunsen	Zinc	2·69
	Sulphuric acid (S G 1 8)	4 43
	Nitric acid (S G 1 4)	7 98
Leclanché	Zinc	2 69
	Sal-ammoniac	4 41
	Manganese dioxide	7 08
Bichro- mate Cell	Zinc	2 69
	Sulphuric acid (S G 1 8)	10·32
	Potassium bichromate	4·04
Chromic acid cell	Zinc	2 69
	Sulphuric acid (S G 1 8)	9 01
	Chromic acid (chromium trioxide)	2·89
Lalande	Zinc	2·69
	Caustic potash	3·3
	Copper oxide	3 37
	(Copper produced)	(2 61)

APPENDIX

TYPES OF VOLTAIC CELLS

IN the following tables will be found details of a number of voltaic cells, which have been invented from time to time since Galvanis' original discovery in 1786. The basis of selection is either historical interest, first invention, or practical utility. Many names not particularly filling these conditions have been omitted.

The author does not pretend to have tried all the cells enumerated, but, where he has, any errors have been rectified, thus applies more particularly to the values of E M F.

It should be understood the author does not guarantee in any way the E.M.F.'s, dates, or data in the table, since accurate particulars are frequently somewhat difficult to trace.

For economy of space the following symbols have been used—

H_2SO_4	= sulphuric acid	Zn	= zinc
HNO_3	= nitric acid	C	= carbon
CrO_3	= chromic acid	Cu	= copper
HCl	= hydrochloric acid	Pb	= lead
Salt	= sodium chloride	Ag	= silver
$\text{K}_2\text{Cr}_2\text{O}_7$	= potassium bichromate	Fe	= iron
CuSO_4	= copper sulphate	Al	= aluminium
ZnSO_4	= zinc sulphate	Pt	= platinum
AmCl	= ammonium chloride	Ni	= nickel
NaOH	= caustic soda	Hg	= mercury
MnO_2	= manganese dioxide	PP	= porous pot
Aq	= water		

a d signifies that air is probably the depolarizing agent by occlusion from the atmosphere, more or less feebly.

USEFUL BOOKS OF REFERENCE

- Electricity and Magnetism* Prof S P Thompson (Macmillan)
Galvanic Batteries S R Bottone (Whittaker & Co)
Piles et Accumulateurs Electriques L Jumeau (Lib Armand Colin, Paris)
Practical Electricity Prof W E Ayrtton (Cassell & Co)
Primary Batteries W R Cooper (Benn Bros)
Primary Batteries Henry S Carhart (Allyn and Bacon, Boston, U S A)
The Voltaic Cell Park Benjamin (Wiley & Sons, New York)

SINGLE-FLUID CELLS

	Anode	Solution and Depolarizer (if any)	Cathode	E M F	Date
Anderson	Zn	Solution of $K_2Cr_2O_7$, HCl, and oxalic acid	C	1.3	1889
Aymonnet	Fe	Aqua regia	C		1886
Bagnaton	Zn	Dilute H_2SO_4 in earth or sand	Cu		1844
Barnett	Zn	Carbonized velvet in dilute H_2SO_4	C	8	1894
Becquerel	Zn	Plates mechanically moved in dilute H_2SO_4	Ag ^{rt}	79	1852
Bellini	Pb ^{ac}	2 parts H_2SO_4 , 3HNO ₃ , 25Aq	C	1.1	1915
Blair	Zn	Concentrated potassium carbonate	Tin		
Boettger	Zn	Moistened magnesium sulphate and salt	C		1867
"	Zn	Ferric sulphate solution	C		1867
Broglio	Zn	Concentrated sodium or potassium bisulphite	C		
Buehn et Trecoche	Zn	Solution potassium bisulphate	Several rods of C		1884
Callan	Zn	Dilute H_2SO_4 and sodium sulphate	Fe		
Chardin	Zn	Solution 1 part HCl, 3Aq, 2 Alcohol	C	1.2	1886
Chuteaux	Zn	In sand Solution $K_2Cr_2O_7$, mercuric sulphate, and H_2SO_4	Crushed C		
Defonville and Humbert	Zn	Chlorine water and 10 per cent HCl solution	C		
Delaurier	Zn	Solution $K_2Cr_2O_7$, H_2SO_4 , sodium sulphate and ferrous sulphate	C		
Desbordaex	Zn	$CuSO_4$ and $ZnSO_4$ mixed	Cu		1844
Duchernun	Zn	Large plates in sea water as electric buoy	C		
Edgar & Milburn	Al	Solution AmCl and HCl	C		
Erckmann	Zn	Dilue H_2SO_4 Rotated discs	Cu		
Fernoy	Zn	Solution, nitrate of soda, $K_2Cr_2O_7$, and HCl	C	1.9	1890

	Anode	Solution and Depolarizer (if any)	Cathode	E M F	Date
Figuer	Zn	Ferric chloride and ferric sulphate concentrated	C	1.5	1863
Fitch	Zn	Chlorate of potash or sodium, and salt or AmCl	C	1.1	
Fouvielle et Deheram	Zn	Binoxide of hydrogen and 10 per cent solution HCl	Cu		1858
Fyfe	Zn	Solution CuSO_4 , potassium nitrate and salt	Fe		1837
Hare	Zn	Spiral plates in dilute H_2SO_4	Cu		1824
Hartmann	Zn	Gauze Porous material in NaOH	Fe or Ag		
Helm	Zn	Salt and alum	C		
Huggin	Tin	Dilute HCl and persulphocyanide of iron	C		1882
Hulot	Zn	Dilute H_2SO_4 (Al roughened in HCl first)	Al		1855
Jablochkoff	Sodium on Cu	Moist paper placed on porous C	C	2.5	1884
"	Sodium	Moist sawdust	C	2.2	1885
Jourdan	Zn	Solution silicate of soda	Vessel of C		1880
Laurie	Zn	Solution of iodine in iodide of zinc	C	1	1881
"	Cadm'm	Solution of iodine in iodide of cadmium	Pt	1.07	1886
Law (a.d.)	Zn	Solution AmCl	Very large C	1.5	1882
La Valette and Delaunier	Zn	Solution zinc chloride	Cu		1845
Leuchtenberg	Zn	Dilute H_2SO_4	C		1864
Maiche	Fe	Dilute HNO_3	Rotating disc of C or Cu	over 1	1874
"	Zn	Solution AmCl	Platinized crushed carbon C	1.25	1870
Martyn Roberts	Tin	HNO_3 S G 1.24	C	2	1867
Mouthiers	Zn	Solution ammonium carbonate	C		
"	Zn	Concentrated ferrous sulphate	C		
Niaudet	Zn	Dilute H_2SO_4	Pb		1867

SINGLE-FLUID CELLS—(contd.)

	Anode	Solution and Depolarizer (if any)	Cathode	E M F	Date
Osbo Premier	Zn	Single fluid bichromate cell, revived by oxygen from mixture of chloride of lime and nickle nitrate	C	2	1891
Pabst	Fe	Ferric chloride solution	C	78	1884
"	Tin	10 per cent solution stannic chloride	C		1884
Poggendorff	Zn	Solution $K_2Cr_2O_7$ and H_2SO_4	C	2	1842
also Chardin, Grenet, Trouvé, Benko					
Pollak (a d)	Zn	Solution of salt or AmCl	Copper plated on C	1 3	1842
Prax	Zn	Electrodes separated by flannel and paper soaked in AmCl	Cu		1857
Pulvermacher	Zn	Zn and Cu wires wound on wood spirally, soaked in vinegar	Cu		
Roberts	Tin	Dilute HNO_3	Cu		1852
"	Zn	Solution of potassium permanganate, potassium bichromate, salt and AmCl	Pb		
Roudel	Zn	Solution 20 per cent HCl (Cu covered at bottom by mud of potter's clay)	C	1 8	1886
Schanschueff	Zn	Mercurial $H_2SO_4 + Aq$	Cu		1860
Schroder	Zn^{H_2}	Solution $H_2SO_4 + HNO_3$	C		
Selmi	Zn	Solution potassium sulphate	C		
Smee	Zn	Dilute H_2SO_4	Cu	1	1867
Stohrer	Zn	Solution alum	Ag^{+}	47	1840
Sturgeon	Zn	Dilute H_2SO_4	C		
Tommassi	Zn	Dilute H_2SO_4	Fe	1 37	1840
"	Mg	Solution of mercuric sulphate with salt	Graphite	1 7	1881
"	Zn	Solution of sodium bichromate with H_2SO_4	C or Pb	1 9	1866
			C		1881

	Anode	Solution and Depolarizer (if any)	Cathode	E M F	Date
Torregiani	Pb	Solution of potassium carbonate	C		1886
Tyer	Zn	Dilute H_2SO_4	Ag^{+}	5	
Volta, also	Zn	Dilute H_2SO_4	Cu	9	1800
Cruikshank, Children, Wollaston					
Walker	Zn	Solution H_2SO_4	C^{+}		1859
Weare	Zn	Solution H_2SO_4 in straw or paper pulp	Cu		
Zahwski	Zn	Salt solution	C		
also Cauderay, Palagi					
Zahwski	Cu	Solution H_2SO_4 and HNO_3	C		1869
SINGLE-FLUID CELLS WITH SOLID DEPOLARIZER					
Bequerel	Zn	Solution salt P P solution salt with lead sulphate	C	59	1846
Bennet (a d)	Zn	Solution caustic potash P P Iron turnings	Fe		1883
Clamond	Zn	Solution AmCl P P ferric oxide and crushed carbon	C	1 2	1874
D'Arsonval	Zn	Solution Zinc chloride P P silver nitrate	Ag	1 15	1881
De la Rue	Zn	Solution AmCl or salt	Ag	1 03	1868
" "	Zn	MnO_2	C		
De la Rue	Zn	Dilute H_2SO_4 P P lead peroxide	Pt	2 4	1843
Denys	Zn	Salt or acid solution P P dilute H_2SO_4 cupric oxide	Cu		1870
Fabri et					
Ravaglia (a d)	Zn	Caustic potash P P crushed carbon	C	1 6	1884
Féry (a d)	Zn	Solution AmCl	Special porous C	1 4	
also le Carbone					
Fortin (a d)	Zn	Solution AmCl P P , crushed carbon	C	1-08	
also Devos, Weber					
Gaiffe	Zn	Solution zinc chloride	Silver chloride fused round Ag	1 02	

SINGLE-FLUID CELLS—(contd.)

	Anode	Solution and Depolarizer (if any)	Cathode	E M F	Date
Heraud	Zn	Solution AmCl	Bag of mercurous chloride round C	1.45	1879
Higgin	Tin	Dilute H ₂ SO ₄	P P MnO ₂ and crushed carbon		1882
Howell	Zn	Solution ammonium sulphate	P P Manganese sulphate, MnO ₂ and crushed carbon	1.6	1879
Lagrange (a d)	Zn	Dilute H ₂ SO ₄	Bag of crushed carbon round C		1852
Lalande	Zn	Solution caustic potash	Cupric oxide round Fe or Cu	98	1881
Lecaniché	Zn	Solution AmCl	P P Crushed MnO ₂ and carbon round C	1.48	1868
Le Roos	Zn	Acidified Aq	P P Manganese peroxide and HCl		1853
Leuchs	Zn	15 per cent caustic potash	P P MnO ₂	1.9	
Marie Davy	Zn	Acidified Aq	P P paste of sulphate of mercury	1.4	1859
Matteuchi	Zn	Solution of salt	P P solution of salt and flowers of sulphur		
Niaudet	Zn	Solution of salt	P P chloride of lime or hyperchlorite of soda	1.6	1879
O'Keenan	Zn	Dilute H ₂ SO ₄	Collodion and lead peroxide on C	2.2	1883
Pabst	Zn	Solution zinc chloride	Zinc oxide paste on C	1.2	1886
Reynier, also Wheatstone, Roberts	Zn ^{Hg}	Solution of H ₂ SO ₄	Lead peroxide in grid of Pb	2.35	1884
De la Rue, Roberts	Zn	Niaudet, Fitzgerald, and Harrison			
Servanow	Zn	Solution of salt and sodium bichromate	Agglomerate, of minium, potassium permanganate and HCl round C	1.8	1886
Sieard and Fallé	Zn	Solution of caustic potash	Silver chloride round C	1.5	
Walter Wilkms (a d)	Zn	Solution of salt, Powdered carbon, alum, H ₂ SO ₄ , K ₂ Cr ₂ O ₇ round	C	2.03	
		Solution of caustic potash	P P crushed carbon		
			Perforated Ni	1.3	1894

TWO-FLUID CELLS

	Anode	Solution and Depolarizer (if any)	Cathode	E M F	Date
Agapin	Zn	Potassium cyanide PP HNO_3	C		1880
Anderson	Zn	Solution of AmCl P double oxalate of chromium and potassium, dilute HCl	C		
Archeveau	Cu	Dilute H_2SO_4 PP HNO_3	C	5	1829
Becquerel	Zn	Saline solution P P CuSO_4	Cu		
Birn and	Zn	Solution of caustic soda, P P aqua regia, ferric chloride, and/or chromic acid	C	2 5	1886
Flaschlacher	Zn	Caustic soda and gum arabic solution P P solution CrO_3 , HCl and ferrous sulphate	C	2 5	1908
Bleack-Love	Zn	Solution of zinc chloride P P bromine in dilute HCl	Crushed carbon C	3	1900
Bottone	Zn	Dilute HCl Layer of sand on carbon at bottom, solution of iodine in potassium iodide	C	2	1900
"	Zn	Dilute H_2SO_4 , P P HNO_3	Al	1 44	1857
Buff	Zn	Salt water, P P concentrated ferric chloride and HCl	C	1 52	
"	Al	Dilute H_2SO_4 , P P HNO_3	C	1 37	1857
Bunsen	Zn	Dilute H_2SO_4 , P P HNO_3	C	1 96	1842
Callan	Zn	Salt solution, P.P concentrated H_2SO_4 , HNO_3 and potassium nitrate	C		1847
Callaud	Zn	Zn sulphate. Gravity Cupric chloride or copper sulphate	Cu	1.	1861
Dale	Zn	Solution of zinc chloride, P P solution of $\text{K}_2\text{Cr}_2\text{O}_7$ and HCl	C		1881
Damell	Zn	Dilute H_2SO_4 , P P PtCl solution	Pt	sug'd	
"	Zn	Dilute H_2SO_4 , P P concentrated CuSO_4	Cu	1 07	1836

TWO-FLUID CELLS—(contd.)

	Anode	Solution and Depolarizer (if any)	Cathode	E M F	Date
Darmon	Zn	Solution of salt, chalk, and mucilage P P ferric chloride and CrO_3	C	1 6	1921
d'Arsonval	Zn	Dilute HCl and H_2SO_4 P P solution HNO_3 , HCl, and H_2SO_4	C	2 2	
"	Zn	Solution of salt, P P. 1. HNO_3 , 1. H_2SO_4 , 1 Aq, saturated CuSO_4	C	1 8	1881
"	Zn	Solution of caustic soda P P solution ferric chloride	C	2 7	1881
Delaurier	Fe	Salt water P P solution of ferric sulphate and H_2SO_4	C		1870
"	Zn	Solution of salt, P P 25 CrO_3 , 25 ferric sulphate, 30 H_2SO_4 60 Aq	C	2 16	1870
Dering	Zn	Solution of salt P P solution H_2SO_4 and sodium nitrate	C		
Dowse	Zn	Solution of AmCl and CrO_3 , mercuric sulphate and HCl P P concentrated solution of CuSO_4	Cu	2.	1867
Duchernun	Zn	Dilute H_2SO_4 P P solution of picric acid and H_2SO_4	C	1 5	
"	Zn	Solution of salt P P solution of ferric chloride	C		
Duffett	Zn	Solution of AmCl P P solution of HNO_3 , CrO_3 , MnO_2 and crushed carbon	C	2	1890
Dun	Zn	Solution of caustic potash Potassium permanganate in hollow porous C	C	1 8	
Dupre	Zn	Solution of salt or potassium bisulphate, P P sodium nitrate, $\text{K}_2\text{Cr}_2\text{O}_7$, H_2SO_4 , Aq	C	1 6	1885
Edgar and Milburne	Al	Solution of AmCl and HCl P P HNO_3	C		
Eisenlohr	Zn	Solution of sodium or potassium bitartrate P P CuSO_4	Cu		1849

	Anode	Solution and Depolarizer (if any)	Cathode	E M F	Date
Ettore	Zn	Solution of AmCl Chlorine gas generated by HCl on chloride of lime in hollow porous C		2 5	
Favre	Zn	Dilute H_2SO_4 , P P solution of CrO_3	Pb	1-35	1871
Fuller	Zn	Water P P $K_2Cr_2O_7$, H_2SO_4 , Aq	C	2 14	
Grenet	Zn	Acidified Aq P P Iron alum	C	1 7	
Gerardin	Fe	in iron turnings P P ferric chloride in aqua regia	C		1866
Goarant de Tonclun	Zn	Solution of AmCl P P solution of $K_2Cr_2O_7$ and H_2SO_4	C		
Grove	Zn	Dilute H_2SO_4 , P P HNO_3	Pt	1 9	1838
Hawkins	Zn	Dilute H_2SO_4 , P P HNO_3	" passive " Fe		1840
also Callan, Schonbein, Maynooth, Turton, and Slater	Zn	Salt solution, P P dilute H_2SO_4 , crushed coke round	C		1871
Highton	Zn	The whole to be boiled for depolarization			
"	Zn	Solution of caustic soda or potash P P MnO_2 , crushed carbon, milk of sulphur, dilute H_2SO_4	C		1872
Holmes and Burke	Zn	Solution of salt P P solution of H_2SO_4 and sodium nitrate	C	1 92	
Kmg, Mendham	Zn	Dilute H_2SO_4 , P P Lead sulphate solution in hypsulphite of soda	Cu	55	1885
Kohlfurst	Zn	Magnesium sulphate Gravity $CuSO_4$	Pb		
Koosen	Zn	Acid solution P P bromine	Pt	1 9	1884
"	Zn	Salt solution P P solution of potassium permanganate and H_2SO_4	C	2	1873
Kousmine	Zn	Solution of H_2SO_4 Gravity, dilute $K_2Cr_2O_7$ at top	C		1890

TWO-FLUID CELLS—(contd.)

	Anode	Solution and Depolarizer (if any)	Cathode	E M F	Date
Lacomb	Zn	Salt solution P.P potassium chlorate, ferric sulphate or chloride, H_2SO_4 and Aq	C	2 15	1871
Leblanc	Zn	Dilute H_2SO_4 P.P. chloric acid	C	1 5	1864
Maître	Fe	Dilute HNO_3 P.P. concentrated HNO_3	C	1 5	1865
"	Zn	Dilute HCl. P.P. stannic chloride	C		
Maquay	Zn 95,	Pb 2, Tm 2, Hg 1, alloyed Dilute H_2SO_4 P.P. solution of $K_2Cr_2O_7$, HNO_3 , H_2SO_4 Sulphur on C	C	1 5	1886
Marron	Zn	Dilute H_2SO_4 P.P. solution of ferric chloride	C		
Mauri	Zn	Solution of salt. P.P. Dilute potassium nitrate, mercuric chloride, and iodine	C		
Mendinger, also Callaud, Lockwood	Zn	Magnesium sulphate Gravity $CuSO_4$	Cu	1 07	1881
Minotto	Zn	Zinc sulphate, sand $CuSO_4$	Cu	1 07	1863
Païne	Zn	Solution of hyposulphite of soda P.P. solution of ferric chloride	C	1 6	1913
Partz	Zn	Solution of magnesium sulphate or salt P.P. magnesium sulphate or salt with CrO_3 and H_2SO_4 crystals fed by gravity	C	2	
Ponci	Fe	Solution of ferrous chloride. P.P. ferric chloride	C	99	
Prevost	Zn	Dilute H_2SO_4 Nitrate of soda and H_2SO_4 in porous hollow C	C		
Reinch	Zn	Dilute H_2SO_4 P.P. aqua regia	Cu	1 5	1881
Reynier, also d'Arsonval	Zn	Solution of caustic soda. P.P. solution of $CuSO_4$	Cu		
Rouillon	Zn	Dilute H_2SO_4 P.P. aqua regia	Ag		
Rousse	Fe	Aq P.P. HNO_3	C	1 2	1866

	Anode	Solution and Depolarizer (if any)	Cathode	E M F	Date
Rowbotham	Fe	Aq P P dilute HNO_3 and H_2SO_4	C	1 3	1897
Schoenbein	Zn	Dilute H_2SO_4 P P HNO_3 and H_2SO_4	C		1842
Slater	Ni	Acidulated or salt aq. P P solution of $\text{K}_2\text{Cr}_2\text{O}_7$	C	1 5	1881
"	Ni	Solution of nickel sulphate P P dilute HCl	C		
Sosnowski	Zn	Solution of caustic soda or potash P P HNO_3 , HCl , and H_2SO_4	C	2 37	1866
Than	Zn	Dilute H_2SO_4 P P HNO_3 and CrO_3	C	1 9	1884
Thomsen	Cu	Dilute H_2SO_4 P P solution of $\text{K}_2\text{Cr}_2\text{O}_7$, H_2SO_4	C	9	1860
Upward	Zn	Aq P P chlorine gas forced on crushed carbon	C	2 1	1886
Watson	Zn	Solution of zinc sulphate and lead acetate Gravity			
Weare	Zn	Concentrated calcium chloride. P P saturated cupric chloride	Cu		
Weymersch	Zn	Dilute H_2SO_4 P P solution of sodium nitrate, CrO_3 , H_2SO_4	C		1890
Wilbrant	Zn	Solution of AmCl P P saturated solution of ferrous sulphate	C	1 8	1882
Wolcott Gibbs	Zn	Solution of salt P P HNO_3 saturated with ammonium nitrate	C		1878

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